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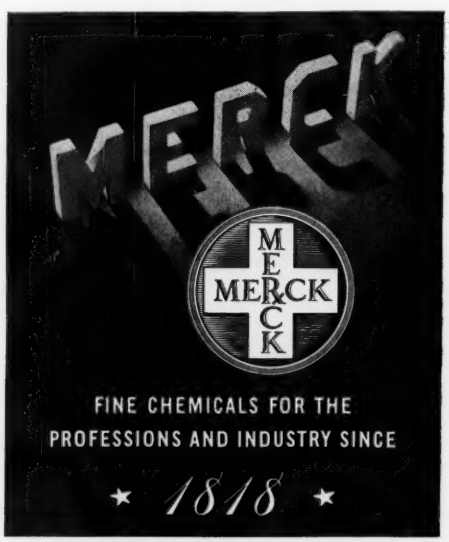

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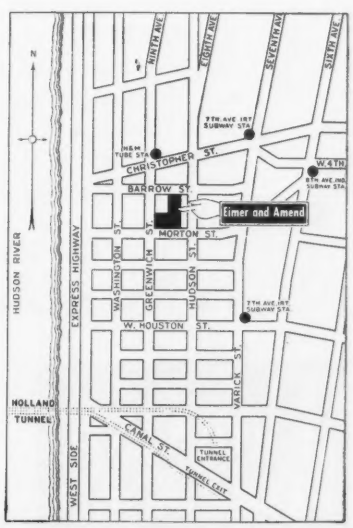

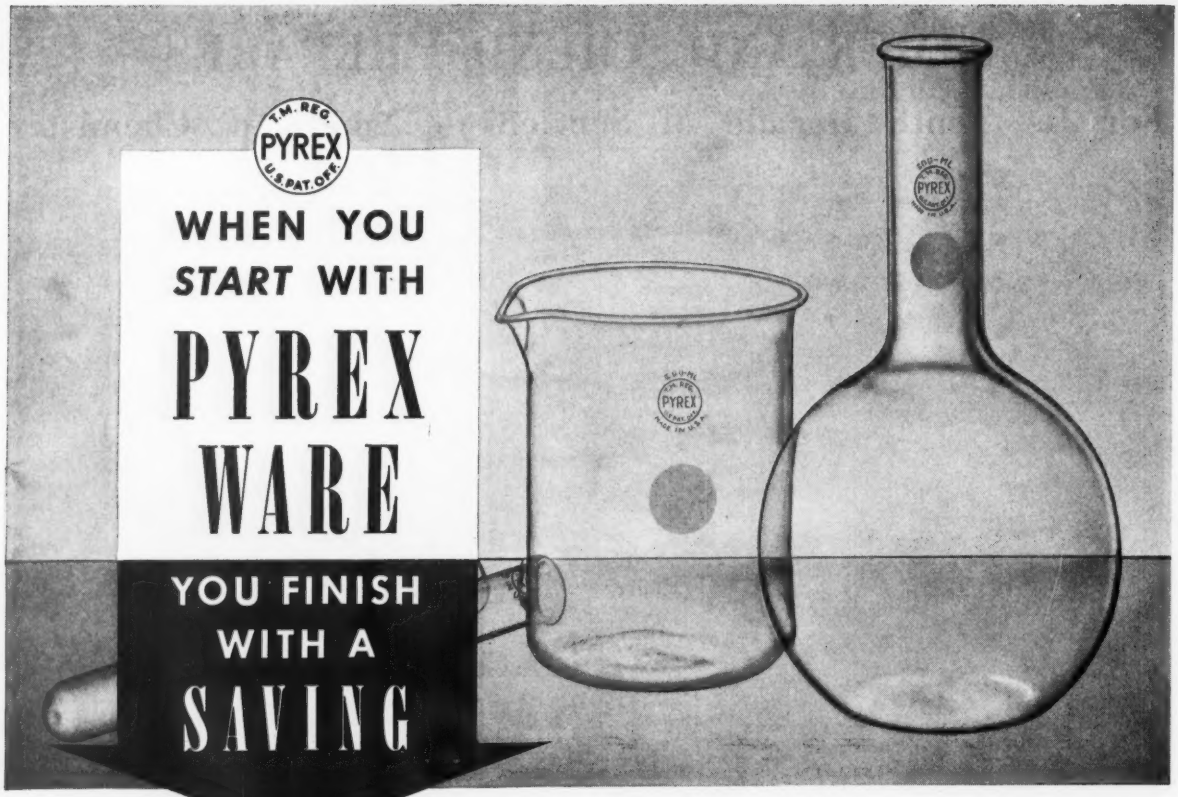

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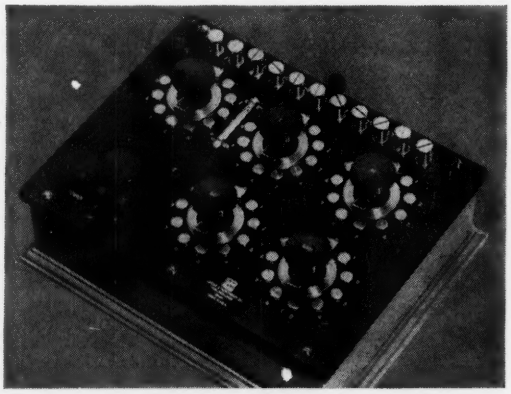
The furnace supplies check temperatures of 150 C to 1000 C; the constant-temperature bath is for lower temperatures. Both are adaptations of our similar catalog-listed equipments.

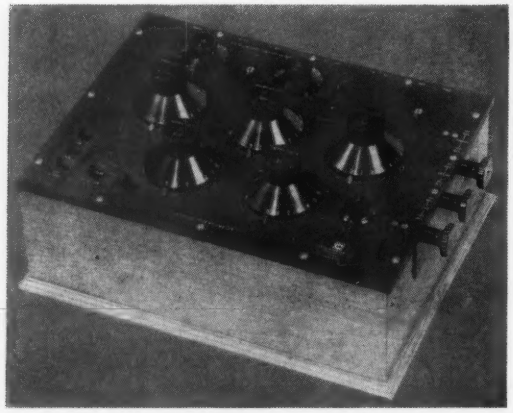
The Wenner Potentiometer is our No. 7559, for precise measurements of low voltages; primarily for thermocouple work; features are wide range, high accuracy and extremely low parasitic emfs, and special protection against effects of humidity on the resistors. Resistance in galvanometer circuit is 13 ohms. The potentiometer has 2 ranges; 0 to 0.11111 volt in steps of 1 μv, with limit of error of ±0.01% + 0.5 μv; and 0 - 0.011111 volt in steps of 0.1 μv, with limit of error of ±0.01% + 0.1 μv. The price of No. 7559 is $1245.00.

The galvanometer used with this potentiometer has a sensitivity of 0.0019 μa per mm at 1 meter, a period of 6.2 sec., and a critical damping resistance of 73 ohms. It is our No. 2285-x, price $115.00.



Mueller Bridge, Type G-1

Wenner Potentiometer



To measure the temperature of the oil bath, we use the Mueller Bridge, Type G-1. Its range is 0-51.111 ohms in steps of 0.0001 ohm; its limit of error ±0.02% or ±0.0001 ohm, whichever is greater. With it, we use a No. 8163 Platinum Resistance Thermometer, having a resistance change of about 0.1 ohm per degree C. The Bridge is $340.00. The thermometer is $150.00, plus Bureau of Standards calibration charge.

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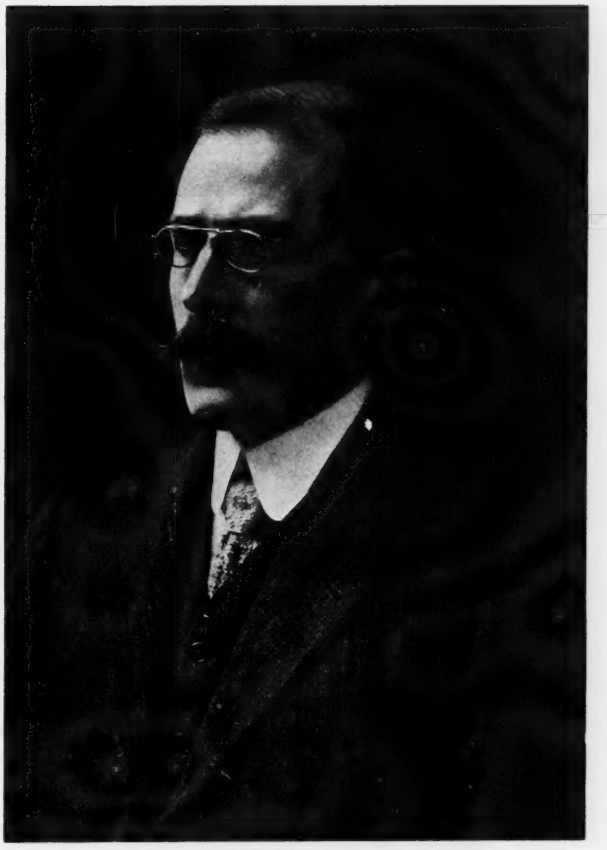

Alfred Walter Stewart
(1880–)

Contributed by Ralph E. Oesper, University of Cincinnati

(For biographical sketch of Alfred Walter Stewart, see page 492.)

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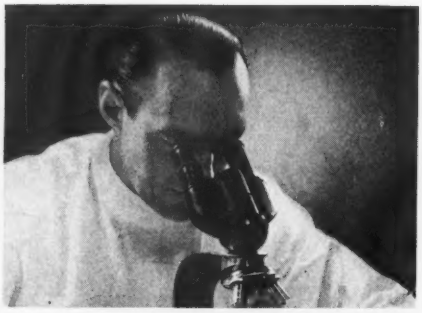
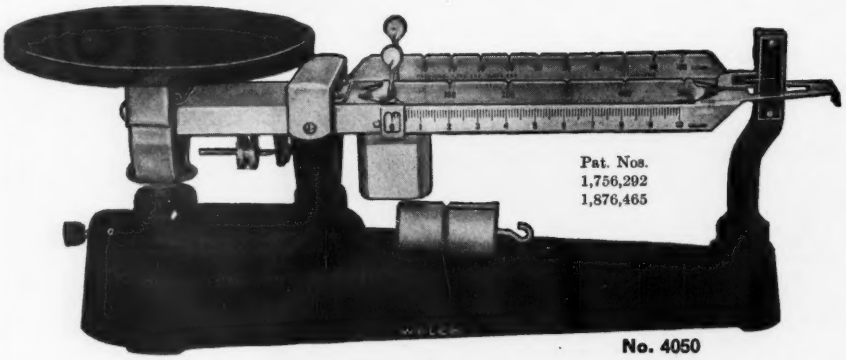
More than an ordinary scale

New TRIPLE-BEAM TRIP-BALANCE *of STAINLESS STEEL*

Cobalite Knife Edges
Agate Bearings





No. 4050

Capacity: 1610 grams

Sensitivity: 0.1 g.

The first triple-beam trip scale was developed by Welch and this newest design contains many noteworthy and valuable improvements.

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Every tiny screw, rivet and nut in this balance is of stainless steel. Laboratory fumes have practically no effect on the stainless steel parts, which were tested in strong chemical solutions for a month's period and showed negligible penetration, with virtually complete corrosion resistance. This insures bright, clear, easily read scales for many years—an exclusive Welch advantage. The use of stainless steel makes possible fine, sharp, easily read graduations on the beams.

BEAM ARREST FACILITATES WEIGHING

A button at the base arrests the swing of the beam, insuring rapid, accurate weighing. This is especially valuable in teaching the novice that the damping device on a comparatively rough scale should be handled gently and easily to avoid throwing the beam and increasing, rather than decreasing, the oscillations.

HARD COBALITE KNIFE-EDGES

The knife-edges are hard, corrosion-resistant Cobalite, a cobalt-chromium-tungsten alloy, used so satisfactorily in industrial applications. Heretofore these were found only in "extra-cost," high-grade analytical balances. Cobalite is used on high-speed cutting tools, automobile exhaust valves, and in almost every place where hard, smooth, corrosion-resistant edges are needed. It provides a life 10 to 20 times that of hardened steel. The bearings for these knife edges are selected quality agate bearings.

INTEGRAL PARTS

In the Welch triple-beam trip scale, the extra weights are provided, and the die-cast base is molded with a semi-circular depression for holding the extra weight. One weight and hanger only provides a capacity of 1110 g. and by the addition of an extra weight the total capacity is brought to 1610 grams.

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The stainless steel cover is provided so that no materials can fall into the agate bearings which support the Cobalite knife-edges. This feature will be particularly appreciated in the chemistry laboratory where so often balances of this type are ruined, and particularly those with ferrous knife-edges or bearings, by some of the salts falling on the knife-edges and into the bearings.

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Editor's Outlook

COMMANDER Ellington tossed the papers onto the desk with a snort and pressed the buzzer.

"Send Mr. Williams in, please." And a little later: "Williams, I hate to haul you onto the carpet like this, but I believe it is necessary. Let's see, how long have you been with this outfit?"

"I came here directly after getting my M.A. at Clearwater College last June, sir."

"Williams, you've done rather well with us. In fact, what I have to say now isn't exactly a criticism of your work. I think we have simply pushed you out a little beyond your depth. When I put you on this present job of yours I didn't realize that it was going to develop into such an important part of our whole Naval Research program. Otherwise I would have chosen a more highly trained man for it. You've been on it for quite a while now and don't seem to be getting anywhere. The fact is that other parts of our program are being held up because of this. I've just been reading your last report and it strikes me you have missed some opportunities. For example, you wasted a lot of time making visual color comparisons when you should have realized that such a method was entirely inadequate. Why didn't you use the spectrophotometer? We have a perfectly good instrument upstairs, you know."

"Yes, sir, I know. But that's just the trouble, and I'm glad to have this chance to relieve my conscience. I suppose I should have confessed it before, but I feel perfectly helpless when it comes to the more complicated instrumental methods. Anything beyond an old-fashioned visual colorimeter scares me. You see, Clearwater College, although it is on the accredited list of the A. C. S., isn't a very rich institution and until very recently has had to depend upon exceptionally good teaching and a lot of simple mechanical ingenuity in order to do a good job of training chemists. A couple of years ago they had a philanthropic alumnus half persuaded to give them quite a lot of money for the express purpose of buying some modern physical and chemical instruments. We seniors looked forward to some interesting work in advanced physical and analytical chemistry. In fact, that was one reason why I accepted a graduate assistantship there for the next year. But I understand that deliveries were rather uncertain and for one reason and another the whole thing fell through. And with the money that was going into the outdoor theater the college wouldn't increase the Department's budget enough to cover the purchases. There were eight of us seniors in the chemistry department and every one of us is now working on some national defense job. Rogers, my roommate, is in one of the ordnance plants and he wrote me the other day that he got into a jam very like this one of mine. It seems they ran into the necessity for some rather high-powered E.M.F. measurements and wanted Rogers to do them. But that was another thing we were cheated out of at Clearwater because the apparatus couldn't be had. So they had to shift a man over from another plant, and I understand there was quite a row over it."

"Well, I suppose I shouldn't be surprised, for civilian administrators never do appear to sense a war-time emergency. It does seem, however, that proper attention would be given to the training of personnel for defense work and supplying the necessary equipment for it. It puts me on the spot right now, in fact. I haven't got a spare Ph.D. I can switch over to this job of yours. If Marino weren't so busy I'd have him put you through a short course in the use of the spectrophotometer, for I think that is the solution to your problem. Maybe you will just have to dig it up out of books, although you'll waste some more time doing that."

"I've got another suggestion, sir, although that will take time, too. They are starting an ESMDT course tomorrow night up at the University, in instrumental analytical methods. I could get into that, I guess, and ask them to get me started on the spectrophotometer as soon as possible."

"Well, that's better than nothing. But get ahead as quickly as you can, for the Department is tramping on my tail to get results and we can't get them until this job of yours is wound up."

Williams started out. "And Williams," added the commander, "if you meet anyone up at the University who seems to pack any official weight tell him the story you just told me. Maybe if the right wheels are started moving they can keep some other poor devil out of the kind of jam you are in."

SINCE the above was written it has been reported that the priorities regulations, which are making deliveries of supplies to college laboratories very difficult, are undergoing revision and that the situation is much brighter. We hope that the principle will soon be recognized that the training of chemists is essentially a defense project.

From the Atlantic City Meeting:

***"If you know something the other fellow doesn't know you can do things he can't do."*—C. A. Kraus**

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What's Been Going On

The Trend in the Use of Antiseptics

THE quest of the chemist today is twofold; he is searching diligently for the improvement of known chemicals and for the discovery of new ones. The search is directed, to a large extent, toward the production of destructive chemicals for use in various types of explosive and incendiary bombs and shells.

Aside from the destruction of the enemy, one is always concerned with self-protection. This is a twofold service involving adequate sanitary control and ample first-aid facilities. It represents the human phase of any armed conflict, and invariably plays as important a role in determining the outcome of a war as do the destructive chemicals.

In this brief consideration of the topic, attention will be given only to the present trend in the use of antiseptics in contrast to that of the last war.

An antiseptic is a substance which is capable of preventing the growth of bacteria, as contrasted with a germicide which actually kills the bacteria. Synonymous with antiseptic is bacteriostat, and with germicide is bactericide.

The use of antiseptics is finally developing along the lines of an exact science. In the past the main objective was complete sterilization of the wound, with little or no thought of the effect of the antiseptic or disinfectant upon the tissue. Until comparatively recently the choice of an agent was so limited that any consideration of specificity or of probable damage to the body's own protective mechanism—even if these factors had been understood—would have been valueless owing to the inability of chemists to produce antiseptics having the necessary characteristics.

In peace time asepsis rather than antisepsis is the operating rule, but in war nearly every wound is bacteriologically dirty and suitable measures must be taken to clean it. During the last war hypochlorites, mainly Dakin's solution, and Chloramine T were the most extensively used antiseptics at first-aid stations and base hospitals. For first-aid dressings, iodine and picric acid led the field.

In the present war there is a decided change. Iodine ampoules are no longer used in field dressing, pads are impregnated with proflavine instead of a mercury salt, and much milder antiseptics than hypochlorites are being used for general wounds, although one chlorine-yielding compound is still advocated officially for surgery.

Most tests which have been introduced to appraise antiseptics take into consideration only killing properties. A number given to an antiseptic, which means something with regard to the compound as a disinfectant, may have no relation to its potency in the body under surgical conditions. When testing antiseptics it is necessary to test them on the particular organism on which it is desired that they shall be effective. The specificity of some antiseptics, especially of the modern ones, is very considerable. The medium in which they are tested also makes a difference. Merthiolate, for example, inhibits the growth of staphylococcus in broth in a dilution of 1:1,000,000, but in blood a strength of 1:1000 is needed to inhibit growth.

The best medium in which to test antiseptics is blood, since it is readily obtainable and of comparatively constant composition. One is able to tell, furthermore, the effect of the chemical on the bacteria and on the human cells, because blood contains active leucocytes. With phenol, as its strength is increased up to a certain point, more and more growth of microörganisms is noted—the reason being that the leucocytes are being killed and the blood becomes a better culture medium. Of course, if the effect of the antiseptic is greater on the leucocytes than it is on the microörganisms, it is valueless.

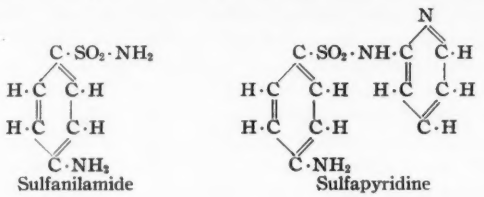
There are new antiseptics in use in this war with which many are already familiar. Foremost of these are sulfanilamide, sulfapyridine, and sulfathiazole. Weak concentrations of these drugs inhibit growth of bacteria in wounds under most conditions, and the British War Office has advocated the routine local treatment of war wounds by dusting 5 to 15 grams of one of these compounds into the lesion.

The action of these drugs is not so much a killing one as an inhibition of the growth of bacteria. The bacteria are not killed by the drug except at high concentrations but their growth is stopped and the leucocytes in the blood permitted to do their work; hence these compounds are not satisfactory disinfectants but are very good antiseptics.

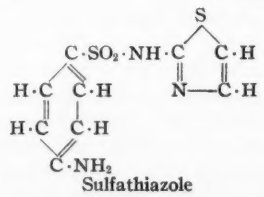
The sulfonamides have limitations, however, in their use. There are a number of conditions which hinder or completely abolish the antiseptic effect of these drugs. The number of live bacteria present has an enormous influence, as has also a large number of dead bacteria. Apparently there is something in bacteria, whether living or dead, which inhibits the action of these drugs. In septic wounds, pus fluid has an inhibitory effect.

Many believe that the best choice of a drug for streptococcal infections is sulfanilamide, for pneumococcal infections sulfapyridine, and for staphylococcal infections sulfathiazole. Actually, sulfathiazole is the most potent of the three, acting better on all microörganisms; sulfapyridine is second in potency, and sulfanilamide last.

In war surgery where these drugs are used extensively other considerations arise. One question is that of solubility because the usual method of applying the drugs is to powder them onto a wound, thus obtaining in the wound a saturated solution of the drug in the fluid. With sulfanilamide the dilution of the saturated solution is about 1:100, with sulfapyridine about 1:1000, and with sulfathiazole about 1:2000. Therefore, although these other drugs are more potent than sulfanilamide, a higher concentration of the latter is obtained in the wound and the ultimate result may not be far different. These chemicals find most of their use in fresh wounds, which contain little matter and relatively few bacteria, rather than under septic conditions.


Sulfanilamide

Sulfapyridine


Sulfathiazole

Sulfathiazole as a chemotherapeutic agent is superior to sulfapyridine in the treatment of pneumococcic pneumonia in that it is just as effective against the microörganism without causing severe nausea. It is also effective in the treatment of staphylococcic infections, such as boils, carbuncles, and similar skin disturbances.

Penicillin has been developed recently, although it has been known for some time. It is limited in its application because of its scarcity, being obtained at present from the blue mold *Penicillium*. As its structure is still unknown, no synthesis can be attempted.

Penicillin has been rated as about four times as effective as sulfathiazole, which permits the use of a much more dilute solution to effect the same protection. Penicillin, moreover, is not

(*Continued on page 487.*)

Samuel Higley, An Early American Metallurgist

FREDERICK H. GETMAN

Hillside Laboratory, Stamford, Connecticut

IN 1766 Sir Edmund Andros was appointed governor of New England and soon resumed the role of petty tyrant he had already so ably filled in the neighboring colony of New York. The autocratic character of his administration is reflected in the words of the Reverend Benjamin Trumbull (*1*) who wrote concerning the régime of Andros:

> "All motives to great actions, to industry, economy, enterprise, wealth and population were in a manner annihilated. A general inactivity and languishment pervaded the whole public body. Liberty, property, and everything, which ought to be dear to men, every day grew more and more insecure."

Into this unhappy period of widespread depression was born in the year 1687, in the tiny village of Simsbury, Connecticut, a lad bearing the name of Samuel Higley (*2*). His parents, who were of sturdy New England stock had, by unremitting toil and dogged perseverance, established a modest home for themselves in the wilderness of the northern part of the colony. Here the boy, Samuel, grew up under conditions demanding the strictest economy and the most diligent application to the assigned tasks of both home and school. He very early showed a marked interest in applied mechanics and, as a pupil in the village school, acquired a reputation for logical and original thinking. At an early age he entered the Collegiate School, which later became Yale College; here he remained for two years, during which time he proved himself a serious student and a young man of more than average abilities. Upon leaving college he returned to Simsbury and for the next three years taught school, while devoting his spare hours to the study of "physick and chyrurgary." From Simsbury Higley removed to Hartford to become the pupil of Dr. Thomas Hooker, a well-known physician of his time, and the grandson of the founder of the city of Hartford. In due time the young man was "approved and allowed to goe on in the practice of physick by the Court." At this early period in American history the average fees received by practitioners of the medical profession were, as a rule, so meager that its members were frequently forced to supplement their incomes by the adoption of some additional vocation. Following this custom, Samuel Higley chose, as his secondary calling, the trade of blacksmithing, thereby enabling him, when the practice of the art of Hippocrates became dull, to earn his livelihood by following in the steps of Vulcan. Upon the death of his father, Higley inherited considerable land near Simsbury, and later, through purchase, acquired additional acreage on a nearby elevation known as Copper Hill. Here, about 1730, he settled and built himself a colonial house which became his home for the remainder of his life. The hill on which this house was built derived the name of "Copper Hill" from the fact that, some years earlier, a vein of copper ore had been discovered about one and a half miles north of the site of Higley's home.

MOUTH OF MAIN SHAFT OF COPPER MINE WITHIN THE OLD NEWGATE PRISON AS IT APPEARS TODAY

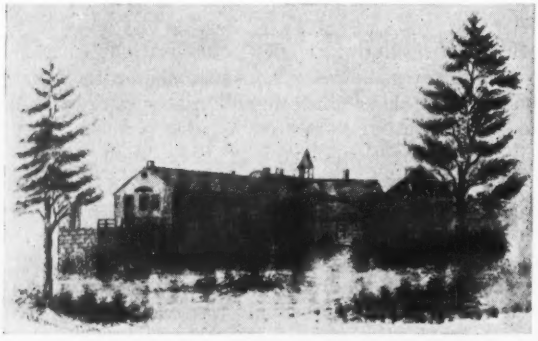
Before considering Higley's association with the copper industry, however, we must digress for a brief review of the developments which later were to enlist the scientific interests of this versatile genius.

While Connecticut has long been known for the wealth and variety of her manufactured products, we suspect that few are aware of the wide variety of those mineral resources which, a century or more since, contributed much to the wealth of her exports. As long ago as colonial days, however, the ores of certain metals such as iron, copper, and cobalt were mined and smelted within her borders, while in other localities appreciable deposits of the ores of such metals as tungsten, bismuth, lead, silver, and nickel were found in workable quantities (*3*).

The first copper mine in the United States was, in fact, the one located near Granby where a vein of copper ore was discovered about 1700. This vein of copper ore at Granby, together with similar veins found elsewhere within the state, are of the type designated by geologists as "contact deposits." Silliman and Whitney (*4*), referring to the copper deposits occurring at both Granby and Bristol, describe them as "contact deposits between the sandstone of the Connecticut River Valley and the older metamorphic rocks, commonly called primary, but in all probability of the paleozoic system." The predominant copper ore

found at Granby was chalcocite (Cu_2S), but along with this, other copper minerals such as bornite (Cu_3FeS_3), cuprite (Cu_2O), chalcopyrite ($CuFeS_2$), malachite ($CuCO_3 \cdot Cu(OH)_2$), and azurite ($2CuCO_3 \cdot Cu(OH)_2$), as well as native copper, were found in appreciable amounts.

In 1707 a company was formed for the development of the Granby mine, but within a few years, apparently because of insufficient knowledge of the technology of copper mining, it was compelled to discontinue further operations (*5*). In 1721 the mine was again operated under lease from the original company and smelting of the ore was undertaken in the neighboring village of Simsbury. Experienced miners and engineers were imported from Germany to superintend both mining and smelting operations, but, notwithstanding this better technical supervision, financial difficulties soon forced the company to discontinue business. After several other unsuccessful attempts to operate the mine, the property was taken over by the colony, in 1773, for use as a federal prison. At that time the mine consisted of two perpendicular shafts sunk through solid rock, one shaft extending to a depth of about seventy feet and the other to a depth of approximately thirty-five feet. From the bottoms of these shafts horizontal galleries had been excavated in different directions, some of them extending four or five hundred feet. A building was erected over the mine for the housing of the prison officials, while the subterranean chambers served as cells for the prisoners. This forbidding place of confinement received the name

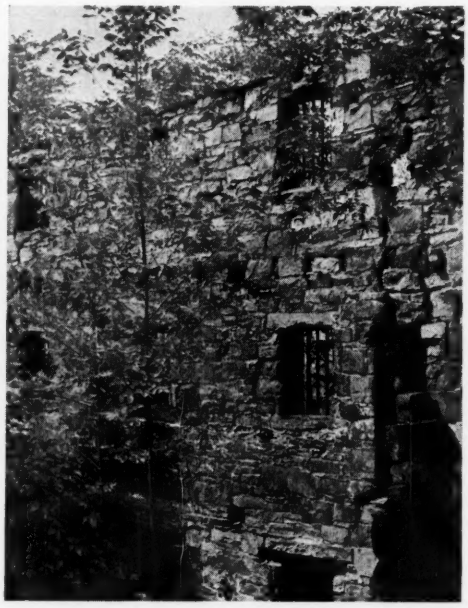


OLD NEWGATE PRISON

From a pencil drawing by George E. Townsend, made in 1863, now in the New Haven Colony Historical Society's rooms. The sketch from which the drawing was made was taken in September, 1861

of the "Old Newgate Prison" and to it Washington consigned many prisoners during the Revolutionary War. Attempts were made to revive the mining of ore with prison labor but without much success, since the prisoners frequently used their picks to facilitate escape. Following the discontinuance of the mine as a prison it was purchased from the state by the Phoenix Mining Company and eventually, about 1830, mining operations were once more resumed only to be abandoned a few years later, never again to be revived.

Having digressed to outline the history of the first copper mine in the United States, we now return to narrate the account of the part played by Higley in the initial stages of American metallurgy. The proximity of the Granby mine to Higley's recently acquired land



RUIN OF WALL OF OLD NEWGATE PRISON

on Copper Hill undoubtedly aroused his scientific curiosity and led him to prospect for copper on his own property, with the result that not only did he discover ore in workable amount, but soon thereafter commenced active mining operations (*2*). According to tradition, "the deposit of copper in the mine was so rich and of such fineness that Higley was in the habit of entering the mine with a pick and obtaining a lump of almost pure metal." This would imply that some of the ore consisted of native copper. Two shafts were sunk and worked, more or less continuously, for nearly fifty years. While the depth of these shafts is not known, they were probably fairly deep, for today, even though choked with rubbish and partially filled with water, an excavation fully twenty feet in depth can be plainly seen. Specimens of the ore were examined by Professor Silliman of Yale College as late as 1870 and reported by him to be "ore of the most valuable description," a statement attested by analysis which showed the average content of the ore to be 10 to 12 per cent of copper. Although Higley may have attempted to smelt the ore, it is believed that he shortly abandoned the project, not only because of the general refractory character of the ore, but also because of the restrictions relative to smelting imposed on the colonies by the British Government. In order to transport the ore to England it was necessary to carry it in wagons over steep mountainous roads to the

Connecticut River where it was then transferred to sailing vessels for transoceanic shipment.

For nearly fifty years Higley operated his mine, during which time many hundreds of tons of ore were shipped to England for smelting. Today bits of copper ore are yet to be found near this mine; these, however, are probably relics of desultory mining operations carried on after Higley's death and believed to have been abandoned about 1830.

The early years of the eighteenth century found the American colonies employing English money in all of their commercial transactions. According to Phelps (*6*):

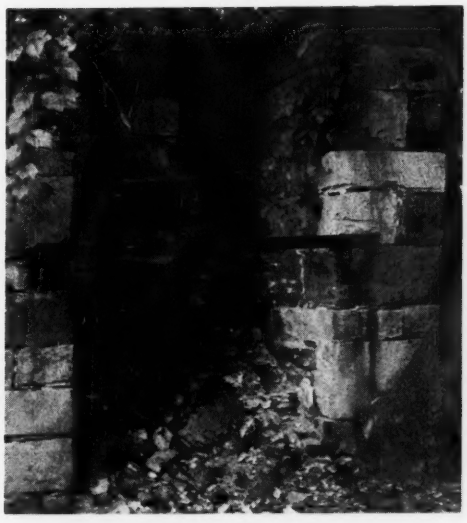
"no public laws had been made by Connecticut to authorize coinage of money, or to specify its value. . . . The foreign trade of the country, which was chiefly confined to England, was principally controlled by her; the balance of trade was continually against us, which prevented the importation of specie."

In view of this condition it occurred to Higley to convert some of the product of his mine into coinage as a remedy for the existing dearth of metallic currency. Just when he commenced the coining of the so-called "Higley Coppers" it is impossible to state with certainty, but they undoubtedly found their way into the trade of the colonies between 1729 and 1737. Five different issues of coins bearing similar designs are known to have been minted by Higley, and of these issues three bore no date. These interesting coins are described in the "Guidebook to the U.S. Mint" (*7*) at Philadelphia in the following words:

"Their Obverses are similar:—A deer standing: below him a hand, a star, and III; around him is a legend enclosed in circles—*Value me as you please.*"

"The Reverse of one variety has three hammers crowned, and the legend—*I am Good Copper*, a hand, some dots fancifully arranged, and 1737."

"The third variety has a broad-axe and the legend—*I cut my way through.* A very few also bear the date of 1739."



REMAINS OF SMELTER AT OLD NEWGATE PRISON

In his "History of Simsbury," Phelps states that "the coin is said to have passed for two and sixpence (42 cents), in paper currency." Several extremely rare specimens are extant today on which the impression of the die is nearly perfect; these are valued as high as seventy-five dollars each by numismatists.

THE HIGLEY COPPER

In 1739, a lawyer by the name of John Read, a brother-in-law of Joseph Talcott, then Governor of Connecticut, made application to the General Assembly for aid to secure from the King of England the right to coin specie. In a personal letter to Talcott he stressed the importance to Connecticut "to procure the King's patent for coinage of copper money from the metal produced from the native ores of the State," and then proceeded to offer not only to undertake the minting of such copper coinage at his own expense, but also to assume any losses which might be involved, provided he should be permitted to retain the entire profits accruing from the proposed enterprise. It is believed that in this effort to secure the right to coin copper currency Higley was associated with Read (*8*). Notwithstanding the urgency of Read's appeal, it was apparently deemed futile by the Assembly to apply to the Crown for a patent covering coinage rights and the proposal was forthwith abandoned. In referring to the Higley "Coppers," Crosby states that:

"these coppers, owing to the fine metal of which they are composed, were much in favor as an alloy for gold, and it is probably due in part to this cause that they are now so extremely rare."

It has been related of Higley that, as a frequenter of the village tavern, he was wont to pay for his dram with coins of his own minting until, eventually, the proprietor complained of being oversupplied with this local currency and refused to accept it in payment for his tavern's much esteemed ale. Some days elapsed before Higley again sought refreshment at the local gathering place of the convivial spirits of the village; when the meeting broke up, and the time for payment arrived, Higley dropped into the hand of the somewhat

apprehensive proprietor a bright, freshly minted copper bearing the inscription, "*Value me as you please,—I am good copper.*" While this legend cannot be substantiated, it is well established that many of the Higley coppers bore the inscription, "*the value of three-pence,*" while some of the later issues bore a suggestion that the bearer should appraise them at his own valuation.

Before the year 1728 Higley had become interested in the manufacture of steel. This interest was probably due in part to his practical experience as a blacksmith, and in part to his familiarity with the opening of iron mines and furnaces at various nearby points. The iron industry was already well established in Connecticut, having been started as early as 1655 by John Winthrop, Jr., at North Haven. In that year encouragement had been given to the new industry by the Assembly at New Haven in a legislative act specifying,

"that if an iron worke goe on within any part of this jurisdiction, the persons and estates constantly and onely imployed in that worke shall be free from paying rates (*9*)".

Quite early in the survey of the natural resources of the colony iron had been found to be quite widely distributed in the region west of the Connecticut River, the chief ores being limonite, hematite, siderite, magnetite, and bog iron. Certain of these ores were subsequently shown by Silliman to resemble the steel ores of Europe, while at the same time it was pointed out by Shepard (*10*) that on analysis such

"ores always consist of the oxide of iron at the lowest state of oxidation and carbonic acid in the proportion of, from 57 to 60 per cent of the former, and 34 to 36 per cent of the latter, together with a proportion of manganese from 0.5 to 1.5 per cent and magnesia and lime in about the same proportion."

He further called attention to the fact that

"natural steel is made at once from sparry iron (siderite, $FeCO_3$) in small blast furnaces, which from their being much used in Catalonia in Spain are called Catalan forges."

The scientific bent of Higley's mind appears to have led him to undertake experimentation with the ores of this character which had been found not far from his home. The success of his early experiments was such as to cause him later to enlist the coöperation of Joseph Dewey of Hebron, Connecticut, who shortly became his partner in the venture. In a statement to the Connecticut Assembly, Higley outlined his experiments and pointed out that

"with great pains and cost, (he) had found and obtained a curious art, by which to convert, change, or transmute common iron into good steel, sufficient for any use, and was the very first that ever performed such an operation in America."

The certificates of several blacksmiths, who had made trial of the steel, and had pronounced it good, were produced in substantiation of the foregoing statement and, therewith, a claim was made for adequate patent protection. After due consideration of the petition, the Assembly issued a patent to Higley securing to him the exclusive privilege for the manufacture of steel for a term of ten years. The fact that the patent was granted to Higley alone leaves Dewey's part in the development of the process open to conjecture. We do not know how long these men carried on the new enterprise, since Higley died before the expiration of the ten-year term of the patent. After Higley's exclusive right to manufacture steel ceased to be in force, twelve years elapsed before application was made to the Assembly for a renewal of the patent; then a license was issued by the General Court granting exclusive rights to Messrs. Fitch, Wyllys, and Walker to manufacture steel by the Higley Process for a period of fifteen years.

Unfortunately we do not know any of the details of Higley's method for the manufacture of steel. It may have involved use of the Catalan forge with the spathic ore so abundant in the neighborhood, or it may have made use of a process resembling the modern cementation method of steel manufacture in which iron bars, after being embedded in charcoal, are subjected to prolonged heat treatment out of contact with air, thus permitting the gradual absorption of carbon by the iron and thereby effecting its transformation into steel. It is the latter process which Swank (*11*) appears to be inclined to favor as the one used by Higley.

Notwithstanding the variety and range of his interests, it should be pointed out that the profession of medicine never ceased to command Higley's allegiance, a fact abundantly attested by the local records of his native village where his name frequently recurs as its sole physician.

While the circumstances surrounding the death of Dr. Higley are shrouded in uncertainty, it appears from such records as are available that he sailed for England in a ship laden with copper ore taken from his own mine and that, during the voyage, the ship was wrecked and all on board were lost. While the exact date of Higley's death cannot be fixed definitely it is believed to have occurred in May, 1737. Thus, at the zenith of his career, shipwreck brought to a tragic end the life of one of New England's early pioneers in the realm of applied science.

We have seen that upon the discovery of copper in his dooryard this man not only applied himself with characteristic energy and perseverance to the development of this possible source of wealth, but subsequently undertook and successfully solved such problems as later presented themselves in connection with the growth of the metal industries in and about Simsbury. With only such rudimentary knowledge of the science of chemistry as was demanded at that time of would-be practitioners of "physick," and with only such empirical knowledge of metals as might have been acquired over the forge of the village smithy, it would have been well-nigh impossible for anyone to have achieved his success without other qualifications, such as undaunted determination, courage, and a generous share of Yankee ingenuity and resourcefulness. The combination of all of these qualifications enabled him, within the space of relatively few years, to achieve

distinction as the successful operator of one of America's first copper mines, as the coiner of Connecticut's first currency, and as the inventor of America's first steel. Today we accord him the distinction of being one of the founders of American metallurgy. It has already been pointed out earlier in this sketch that Higley was born at a time of nation-wide depression. That this condition continued to exist throughout his entire life is evident from the following historical reference to the America of pre-revolutionary times:

"As the country enlarged, and lucrative trade and manufacturing interests increased, the English Government was casting jealous eyes at every movement that men of affairs on American soil were making to supply the colonist's necessities. From merchants and manufacturers who consulted their selfish interests came constant complaints to the Crown, and Parliament had passed oppressive and stringent laws of trade. England was already declaring 'that the erecting of manufactories in the colonies tended to lessen their dependence upon Great Britain,' and was laying a heavy hand upon the western colonies through these restraining laws. It finally came to pass, a few years later, that the manufacture of iron and steel was entirely prohibited, and . . . forges and furnaces in the colonies were declared by the Home Government common nuisances. Thus she was unwittingly maturing and sprouting seed, which, in after years, developed open rupture and revolution."

It thus becomes apparent that Higley's achievements deserve the greater credit because of the fact that his successes were won despite the Crown's discouragement of both free enterprise and industrial development.

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A USE FOR CO_2

THE importance of knowledge about spontaneous combustion and the interest in uses of carbon dioxide make it appropriate to reprint the following story[1]:

"As spontaneous ignition of hay is a leading cause of barn fires in agricultural states, the possibility of control by smothering with CO_2 seems to justify some attention.

"Spontaneous heating and ignition of hay is one of the most elusive of fire waste causes, as actual cases are rarely reported until after fire has either reached an advanced stage or resulted in complete loss. It is difficult to simulate actual conditions of overheating for the purpose of experimentation; therefore, the only possibility of testing the efficiency of CO_2 rested in the chance that an actual case would be reported in time for a test to be made.

"Early on the morning of July 31 we received a telephone call from a county agent who stated that a barn in his county was in grave danger from overheated hay. The tenant on the farm noticed a strong odor coming from the barn at the time he started the morning feeding. After going into the mow, he noticed that vapor was pouring from a flue in the highest level of the hay. The barn was of frame construction, 42 by 70 feet. The mow extended to the ground level in the center and was flanked by a 12-foot feeding space on all sides. Of the 150 tons of chopped hay contained in the mow, a few loads of alfalfa had been put in early in June, and the balance, all clover, had been chopped during the first week in July.

"Our first undertaking after arriving at the scene was to check all parts of the mow in an effort to establish boundaries of the section which appeared to be heating. Planks were laid on the hay to guard against mishap in case burning pockets were discovered. Preliminary temperature tests were made by forcing a 1/2-inch round steel rod into the hay at 10-foot intervals. The rod was first inserted vertically, and was examined for signs of heating after each test. The hottest hay was found to be within a space approximately 10 by 14 feet. After the heated area was localized, the test rod was inserted horizontally at different distances from the ground, to determine the level at which the temperature reached a maximum. The hay near the ground was cool, and signs of excessive heat were not evident until the rod was inserted about 10 feet above the ground level, or 12 feet below the highest part of the hay.

"A thermometer was lowered through one-inch gas pipes which had been driven into the heated hay. . . . Temperature readings taken soon after noon ranged from 180° to 190°F. As most authorities agree that the hay should be removed as soon as the temperature reaches 190°F., plans were made for removing the hay from the heated section. The highest reading taken in the afternoon exceeded 230°F.

"A serious problem arose when the decision was made to remove the hay. The wide space around the sides of the barn above the feeding space was well filled with dry hay. To move the heated hay conveniently it was necessary to cut a hole in the ceiling over the feeding space, and several loads of dry hay had to be moved before this could be done. It was also necessary to call a local fire truck and to lay 500 feet of hose from the water supply. The use of carbon dioxide became valuable in holding the temperature down during the five hours which were necessary for preparation to remove the hay.

"Three one-inch pipes were put down in the heated area in spots where the temperature readings were highest. The equipment consisted of several 20-pound drums of CO_2, a pressure regulating valve, and 50 feet of hose. . . . The hose was placed alternately in the three pipes and it was found that each application reduced the temperature in the vicinity of the pipe about 100°F. The hose was changed from one pipe to another at 20-minute intervals and thus the temperature was kept well below the danger point. These applications were begun about noon and were continued until 5:00 P.M.

"The fire truck equipment was finally assembled at about 5:00 P.M. and removal of the hay began. Glowing embers were noticed soon after the first three or four feet of hay were removed. There was occasionally sufficient heat to cause a small blaze. A fire hose was played on the heated area as needed to keep the fire under control. Fire and water damage was limited to the few tons of hay removed from the heated section of the mow."

[1] KEENEY, "Use of CO_2 in the control of hay mow fires," *Agr. Eng.*, **22**, 176 (May, 1941).

The Electron-diffraction Method of Determining the Structure of Gas Molecules

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INTRODUCTION

THE quantitative study of the structure of molecules is such a new development in the history of chemistry that it is not surprising that little attention is devoted to it in most high-school and elementary college courses. In the opinion of the authors, however, it deserves attention. Discussion of the structure of molecules excites the interest of the student, and creates in him a feeling for their reality. When correlated by a skilful teacher with the physical and chemical properties of compounds, it enables the student better to understand and remember these properties.

Electron-diffraction experiments are an important source of structural information. In this paper we outline the method by which this information is obtained, and give a few of the results. Other results will be described in later articles.

HISTORY

The development of the theory of a science is largely a matter of the proposal and test of models which have properties similar to those experimentally observed. For example, many properties of gases were accounted for by considering the gases to be assemblages of very small, perfectly elastic particles in constant motion; other phenomena were predicted on the basis of this model and verified by later experiments on gases. In the study of light two especially useful models have alternately gained favor. Huygens explained refraction and similar phenomena by considering light to be an advancing wave pulse; Newton, who had already achieved great success in the field of mechanics by treating bodies as agglomerations of particles, preferred to think it composed of moving corpuscles. Though the great weight of Newton's authority silenced opposition for over a hundred years, there was a weakness in his theory—the explanation of the phenomenon of diffraction.

The diffraction of light was discovered about the middle of the seventeenth century by the Jesuit Francesco Maria Grimaldi, a professor at the University of Bologna. In his "*Physicomathesis de Lumine Coloribus et Iride*," published in 1665, he stated that he had observed that the shadow of a hair in a narrow beam of light and the image of a small hole on a distant screen are larger than would be expected if the propagation of light could be indicated simply by drawing straight lines. Shadow fringes appear just outside the geometrical shadow. The name "diffraction" which he gave to the phenomenon comes from the Latin *dis* + *frangere*, and denotes a "breaking apart" of the light.

Experiments such as those made by Grimaldi influenced the brilliant and versatile English physicist Thomas Young in 1802 to revive the wave theory; he calculated some wave lengths of light from Newton's data. Thus the bending of light around corners was explained as a general property of waves; it bends less than the waves to which we are ordinarily accustomed because the wave length is shorter. Even sound tends to travel in straight lines; it is difficult to hear a high-pitched note from behind an obstacle. Young's work was met with ridicule; he abandoned physics for a long period, during which time he made important contributions to the deciphering of the Rosetta stone, so that he now shares with Jean Champollion the honor of having found the key to the Egyptian hieroglyphics. In the meantime his theories were perfected by the French physicist Jean Fresnel, who established the wave theory on a mathematical basis and caused a reversal of opinion in its favor.

Maxwell's development of the electromagnetic theory of light in the seventies showed that the vibrations consist of electric and magnetic field vectors, which do not require a solid for their transmission. The main objection to the transverse wave theory was therefore removed. But in 1905 Einstein, from a consideration of the laws of radiation, enunciated a new kind of corpuscular theory, according to which light is emitted from a radiator in quanta of energy inversely proportional in magnitude to the wave length, and work on the interaction of light with matter established the correctness of his views.

The upshot of the controversy between the advocates of the wave model and the particle model is that light partakes of the qualities of both; both conceptions are too rough to be entirely applicable.

Some twenty years later this dualism of character was carried over to the electron. The discovery of the diffraction of electrons by matter was first clearly foreshadowed in the doctorate dissertation of L. de Broglie (*1*) in 1924, in which he formulated the concept of waves associated with all material particles. The wave length of the particle is given by the relation

$$\lambda = \frac{h}{mv}$$

where m is its mass and v its velocity. The quantity h is a universal constant of nature, equal to 6.63×10^{-27} erg sec. In confirmation of this theory diffraction experiments have now been carried out on beams of electrons and protons, which are found to behave in the same way as light rays, gamma rays, and X-rays, so far as diffraction is concerned.

The chief modern methods of investigating molecular structure are the measurement of moments of inertia from infra-red spectra, the determination of crystal structure by X-ray methods, the study of Raman spectra, the measurement of electric dipole moments, and the diffraction of electrons by gases. In all of these except dipole-moment measurements the phenomenon of diffraction plays an important part. In spectroscopy it enables us to divide the light into its various wave lengths by the interference of the component parts of a wave train. In the diffraction of molecules or electrons the various atoms in the path of the primary beam become centers of radiation, and the effect of a superposition of spherical waves is observed. Since in the second case only a finite number of centers of radiation are involved, the two phenomena are not quite alike in nature, and the second has sometimes been termed "interference." Professor G. P. Thomson has proposed the descriptive name "interfraction."

Though it deals with interactions which are in essence more complicated, the science of the study of the structure of matter through the diffraction of X-rays by crystals was discovered and developed before the science of electron diffraction. Röntgen, and after him many others, tried without success to diffract X-rays; they failed because the shortness of the wave lengths was not appreciated. But seventeen years after their discovery it was found that X-rays could be diffracted by crystal lattices. The first photograph was taken, on the suggestion of von Laue, by Friedrich and Knipping in 1912 (*2*); the first structure analysis, that of NaCl, was given shortly afterward by W. H. Bragg (*3*). The improvement in technic due to the use of X-ray tubes in medical diagnosis and therapy was doubtless a factor in the discovery of these phenomena before those of electron diffraction. The science of X-ray analysis developed rapidly, and remains one of the chief sources of information for structural chemistry.

In 1929 Debye and co-workers (*4*) published a preliminary account of experiments on the scattering of X-rays by gases. Though the data are more easily interpreted than those obtained from a crystal, this branch of X-ray diffraction had been neglected up to that time. Instead of spots, there appear on the film one or two broad rings, the position of which is given by a formula derived many years before by Ehrenfest (*5*) and by Debye himself (*6*):

$$I(s) = \sum f_i f_j \frac{\sin sr_{ij}}{sr_{ij}}$$

where $s = 4\pi/\lambda \sin \psi/2$, ψ is the angle between the incident and scattered ray, λ the wave length, r_{ij} the interatomic distance between the i^{th} and j^{th} atoms, f_i the scattering power of the i^{th} atom, and the summation is over all the atoms of a single molecule. In this way Debye was able to estimate the Cl—Cl distance in CCl_4 and to verify the chemical identification of the cis and trans forms of dichloroethylene. The method did not promise, however, to be a very satisfactory tool for the study of molecular structure, since the number of intensity maxima obtained on the photographs was very small and the period of exposure required was long (several days).

The first experiments in electron scattering, by nickel surfaces, were described by Davisson and Kunsman (*7*) in 1923 and by Davisson and Germer (*8*) in 1927. Further application to the investigation of crystals was made by G. P. Thomson (*9*), who showed that reflections from thin foils of metals, such as gold, silver, and aluminum, obeyed the Bragg law. The complete theory of the scattering of electrons by atoms was developed soon after, with the aid of the newly discovered quantum mechanics, by Mott.

Some work on the diffraction of electrons by crystals was carried out by H. Mark (now of the Brooklyn Polytechnic Institute) and R. Wierl in Ludwigshafen (*10*). Wierl then performed the first experiments on the diffraction of electrons by gas molecules (*11*). A detailed account of this pioneer work appeared in the *Annalen der Physik* in 1931 (*12*). In his introduction to that paper Wierl remarks that of the various methods which were then in use for determining the structure of molecules, that which came nearest to giving direct information on individual molecules was the X-ray diffraction of crystals. Even here, however, the effect of individual molecules is screened by the effect of the lattice, and complications such as temperature effect, mosaic structure, and zero point energy are inherent. The best way to avoid these complications, he said, is to investigate molecular vapors. But since electron-diffraction experiments on thin metal films showed that an exposure of a few seconds with electrons gave the same intensity on a film as one of several hours with X-radiation, the outlook for gas investigation by means of electrons was more promising. The remainder of the present paper is concerned with this topic.

A great advantage of the electron-diffraction method is that there is little interference from wavelets originating from different parts of the same atom; the scattering of the electrons is effected primarily by the nucleus, and the method is therefore well adapted to the study of internuclear distances. Moreover, exposure times are small, and reliable methods have been developed for interpreting the photographs.

For three or four years after 1930 there existed general skepticism as to the reliability of electron-diffraction results. This was due mainly to the existence of a discrepancy of about four per cent between the values of interatomic distances in gas molecules reported from electron diffraction and X-ray studies. The skepticism regarding electron diffraction was fostered in articles and lectures by the investigators who had used the X-ray method for gases. Ultimately, however, it was shown conclusively (*13*) that it was the X-ray results which were wrong.

In his papers Wierl discussed the structure of a great number of molecules. He measured accurately the single, double, and triple bond carbon-carbon distances, and found that carbon atoms in propane, butane, pentane, and hexane make bonds at approximately the

tetrahedral angle. He was able to show that the pictures of 1,2-dibromoethane and 1,2-dichloroethane could not be accounted for by the assumption of free rotation about the carbon-carbon bond. On the whole, his investigations were thorough and extensive, and they showed the way for later workers in the field. His death when he was still a young man cut short a brilliant career.

Since that time several electron-diffraction machines have been built, and technic has gradually improved. The invention of the radial distribution method (*14*) of interpretation of the data gave an independent and objective method for the determination of the interatomic distances. Nowadays structures are deduced from photographs which yield a great deal more data than did the early ones; there have been improvements in the measuring of the photographs and various refinements in the theory such as the inclusion of a factor to take care of the thermal motions of the atoms. Work in this country has been carried out notably at the California Institute of Technology, from 1930 on, the first apparatus other than that used by Wierl having been built there by Dr. L. O. Brockway from information given one of us (L. P.) by Wierl at Ludwigshafen in 1930.

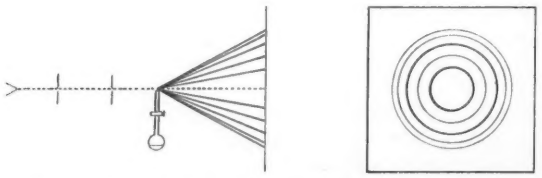

FIGURE 1.—THE ELECTRON-DIFFRACTION EXPERIMENT

EXPLANATION OF THE PHENOMENON

The electron-diffraction experiment is illustrated diagrammatically in Figure 1. A high-velocity electron wave intersects a molecular beam at right angles and is scattered through a solid angle. The resultant intensity of scattering is recorded on a photographic film. Figure 2 is a photograph made with carbon tetrachloride vapor.

In order to show the analogy between the diffraction of light and that of electrons, we shall discuss briefly some easily observed phenomena which are known in physics as examples of Fresnel diffraction.

Light from an arc lamp or from the sun is focused by means of a lens on a pinhole (which may be placed, say, over the keyhole of a door) and the divergent beam is caught on a white screen in a well-darkened room. If objects are now placed in the beam between the pinhole and the screen, diffraction fringes may be observed at the edges of their shadows. If dust is scattered in the light, the shadow of each particle is surrounded by colored rings. The effect of placing another pinhole in the beam is shown in Figure 3. Concentric light and dark rings are observed around a central image, which itself may be light or dark, depending on the diameter of the secondary pinhole and its distance from the screen.

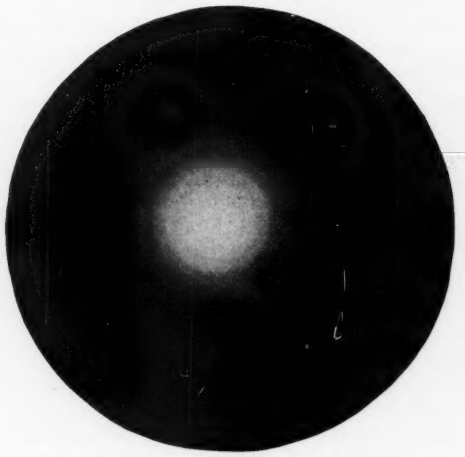

FIGURE 2.—ELECTRON-DIFFRACTION PHOTOGRAPH OF A GAS

Other more familiar examples of the diffraction of light are the halos which are often seen around the moon or the sun. The large rings colored red on the inside which appear at 22° and 46° from the central disc are caused by refraction from ice crystals in high clouds; these effects are particularly prominent in polar regions. Diffraction halos are always closer than 22° to the sun and, when colored, are red on the outside. They arise from diffraction by small drops of water, which individually have the same effect as the circular opening already mentioned. Their action is illustrated in

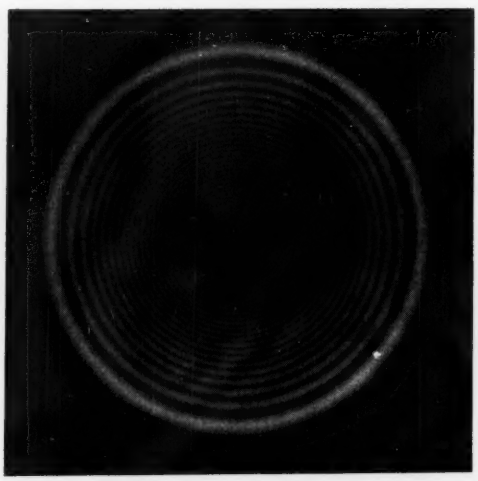

FIGURE 3.—DIFFRACTION OF VISIBLE LIGHT BY A PINHOLE

Figure 4. The angle of diffraction of light, like that of electrons, is dependent on the wave length, and short wave lengths are scattered least. Thus if in the figure

the three arrows coming from each particle represent red, green, and blue light, the observer will receive blue light from *C*, green from *D*, and red from *E*. The effect seen can be represented by rotating the diagram about a vertical axis through *B*. If the conditions in the sky are not uniform, the halo will not appear to be circular.

According to R. W. Wood (*15*), diffraction halos may be produced by viewing a source of light, such as a candle, through a plate which has been dusted with lycopodium powder, or through a large spherical flask, wet on the inside, which has been partially evacuated.

Thomas Young made an early practical application; he invented a wool grader involving the determination of the size of the fibers from the width of the diffraction pattern obtained on passing a beam of light through the wool.

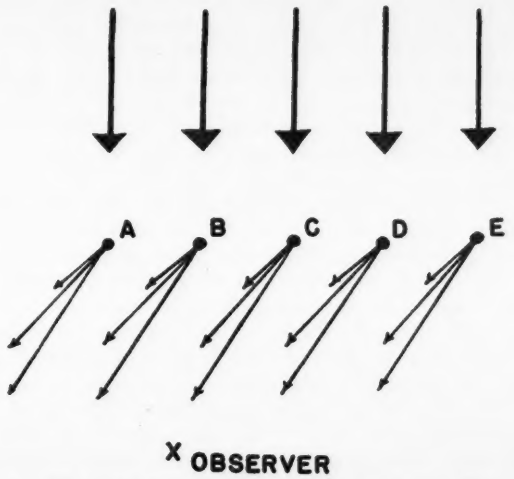

FIGURE 4.—TO ILLUSTRATE THE FORMATION OF A DIFFRACTION HALO

In photographs taken through thin sheets of solids sharp rings are observed; the interpretation here follows the Bragg law—that is, the electrons are reflected from the planes of atoms in the crystals as if from mirrors. Figure 5 shows a transmission photograph of solid stannic oxide. In Figure 2, which is for carbon tetrachloride vapor, rather diffuse concentric rings are observed about a central image. For the case of diffraction of vapors, the intensity follows the formula previously given for the diffraction of gases by X-rays.

In the derivation of this equation account is taken of the fact that the molecules are oriented in all possible directions.

The electron waves strike a cloud of molecules which are emerging from a tiny pinhole perpendicular to the beam. The electrons are perturbed by the electric field produced by the nuclei of the atoms in the molecules and are scattered in all directions, still keeping their wave character. This process takes place so quickly that the motion of the molecules themselves has no effect. The waves scattered from the different atoms interfere and reinforce one another in such a way as to produce a series of concentric diffuse rings on the photographic emulsion.

A graphic illustration of the interference of waves is

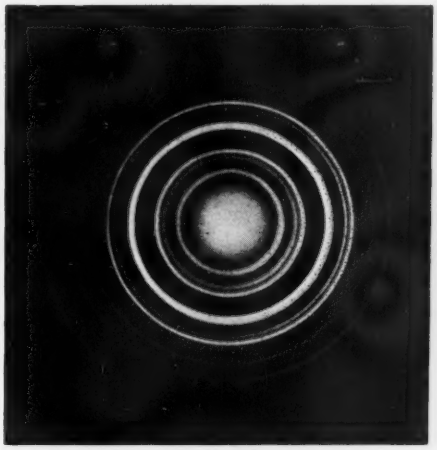

FIGURE 5.—ELECTRON-DIFFRACTION PHOTOGRAPH OF A SOLID

given in Figure 6. Waves from two sources are set up on a water surface. At some points the effect of the waves cancels out so that there is no resultant disturbance; at the maxima, however, the amplitude is twice that of the component waves. The waves proceeding from the different atoms of a molecule interact in just this same way, except that in this case there are spherical waves and, moreover, the effect is aver-

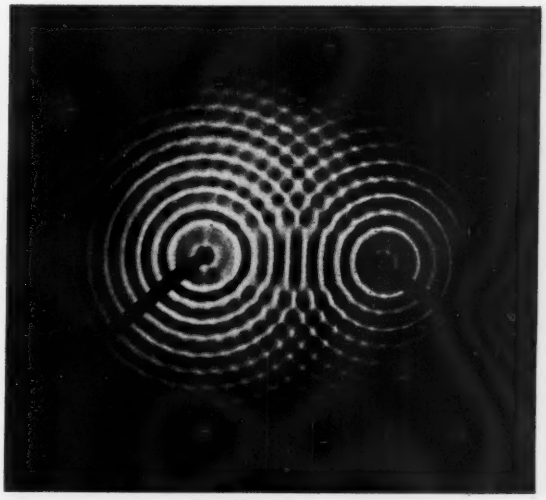

FIGURE 6.—INTERFERENCE OF WATER WAVES

aged over all the different orientations of the molecules. The various molecules are so far apart, relative to intramolecular distances, at the pressures which obtain in the

diffraction chamber at the time of exposure, that the interaction between waves coming from different molecules may be neglected.

Actually this regular kind of interference, the only one of interest to the student of molecular structure, is not the only phenomenon which occurs during an exposure. Some of the waves are scattered from one atom and then from another—this "multiple scattering" is avoided as much as possible by keeping the pressure low. The electrons may also transfer some of their energy to the molecules they strike, and become slowed down; this kind of scattering is called "inelastic." Moreover, X-rays are produced when the electrons are stopped at the edges of the collimating pinholes and at other parts of the apparatus. The effect of all

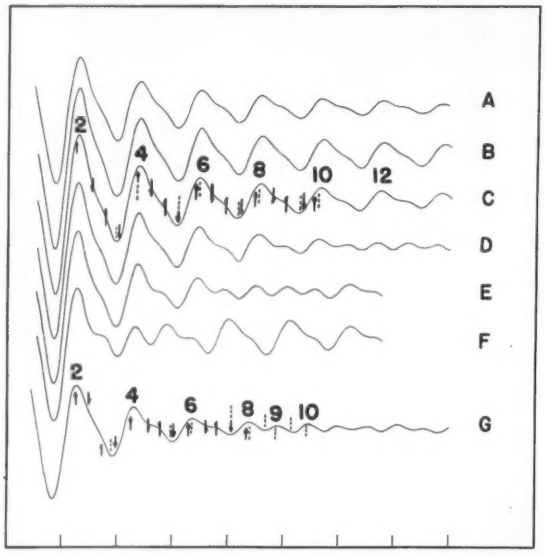

FIGURE 7.—THEORETICAL CURVES FOR A SIMPLE TRIATOMIC MOLECULE (NITROUS OXIDE)

The abscissa represents the distance from the center of the photograph; the ordinate, the calculated intensity of blackening

these occurrences is to produce a dark background on the negative, strong at the central image and decreasing rapidly toward the edge. This background may obscure some of the features which are due to the molecular scattering, but it does not appreciably change the nature of the diffraction pattern. P. Debye (*16*) has shown that by rotating a heart-shaped sector before the film during the exposure it is possible to compensate for the background.

The positions of the rings on the photographs are measured on a comparator. The negative is held on a ground glass screen, illuminated from below, over which move two pointers which can be placed on the apparent intensity maxima and minima of the photograph. The diameter of the rings can then be read to hundredths of a centimeter on a sliding scale. Though it is also possible to measure the photographs by means of a microphotometer, this method is less satisfactory, since the rings are much less prominent on the microphotometer record than they appear to the eye on the original photograph.

The "visual method" of interpretation of electron-diffraction pictures developed by Wierl is generally used today. The first step is the choice of a reasonable model for the molecule which is being studied. The information influencing such a choice may come from various sources, among them spectroscopy, crystal structure, dipole moments, etc. Theoretical scattering curves are then computed by means of the formula given above, and the appearance and the position of the intensity maxima and minima are compared with those observed. If the model is that of a diatomic molecule, the curve will simply be that of a damped sine wave, and comparison between the theoretical curve and the measurements on the photograph will give directly the internuclear distances of the molecule. If the model contains two internuclear distances, as does, for example, that of the linear molecule nitrous oxide, the theoretical curve will consist of a superposition of two sine waves, which will add together and produce a more complicated curve. Curve *A* in Figure 7 is of this type. It gives the calculated intensity for a model of nitrous oxide (*17*) in which the central nitrogen atom lies midway between the two others. Curves *B–F* are for models with the central atom somewhat displaced from this position. The arrows, which represent the experimental measurements, are drawn through an acceptable curve.

If the distances in the model have all been chosen too large or too small by the same proportion, a change in scale in the plotting of the theoretical curve will give agreement with the experimental points; if the model is distorted from the shape of the true molecule, however, this will not be possible. The task of an investigator in this field is to find a model which fits the data, and then to show that no other reasonable model will serve. In doing this he often makes use of the appearance or the relative heights of the various features of the intensity curve.

No numerical estimations of intensity are necessary for the application of the visual method. A more direct method for interpreting the photographs, which does make use of intensities, was introduced by Pauling and Brockway in 1935. They plot the function

$$D(r) = \sum I_k \frac{\sin s_k r}{s_k r}$$

against r. The I_k's are the estimated intensities of the maxima and minima of the rings observed on the photographs, and the values for s_k are obtained from the measurements of the diameters. Such plots are shown in Figure 8. Each curve is a wave-like function, in appearance somewhat like the theoretical curves discussed above. It can be shown that the abscissas of the peaks of the maxima correspond to interatomic distances in the molecule. The positions of the vertical black lines drawn under the curves give the lengths of distances in the model finally decided upon. The height of a line is proportional to the coef-

ficient of the corresponding term in the intensity formula. It is, of course, difficult to estimate accurately the intensity of the blackening of the various rings, but it was found that estimates made by an experienced observer lead to satisfactory radial distribution curves. There is no mechanical method of assigning the distances found to the various parts of a complex molecule, but, since atoms have rather well-defined radii for different types of bonds, it is generally possible to identify them without great difficulty. (For example, the C—C single bond distance is usually close to 1.54A. The double bond distance is about

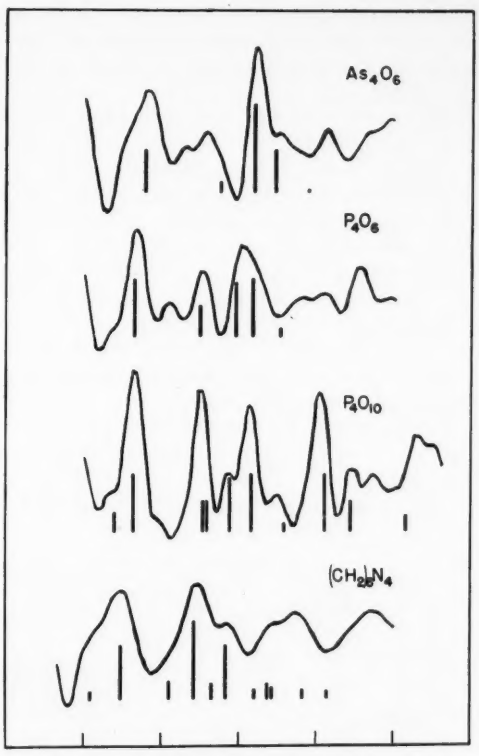

FIGURE 8.—RADIAL DISTRIBUTION CURVES

1.33A.) Usually one can determine two or three interatomic distances by this method. A start is thus obtained on the structure, which is then investigated further by means of the visual method.

THE APPARATUS

A photograph of the second electron-diffraction apparatus built by Dr. L. O. Brockway at the California Institute of Technology is shown in Figure 9. The cathode, which is insulated from the rest of the apparatus, is at the right center. It and the table near it are charged to a potential of about 40,000 volts during operation. A glass tube containing the liquid, the vapor of which is to diffract the electrons, may be seen between the metal supports of the horizontal tube. To the left is a drum containing a wheel which carries five films and a fluorescent screen. These can be rotated successively into place by means of a hand magnet.

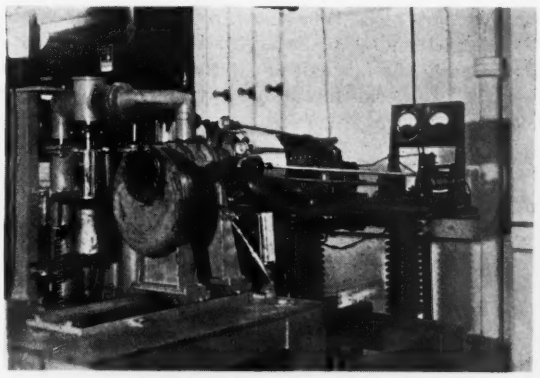

FIGURE 9.—ELECTRON-DIFFRACTION MACHINE AT THE CALIFORNIA INSTITUTE OF TECHNOLOGY

The cathode assembly is shown in Figure 10. *A* is a fine tungsten wire bent into the shape of a V, which is at high potential and heated by a small current. It emits electrons, which move off to the right. The rest of the apparatus, which is at ground potential, serves as an anode. *B* is a focusing cup placed a centimeter or so from the filament and kept at a potential about two hundred volts negative with respect to the filament; it provides a field which tends to sharpen the beam, and does not allow electrons of low velocity (and therefore long wave length) to pass. There are a series of adjustments so that the filament may be moved with respect to the bias cup, and the whole assembly may be moved in the diffraction chamber. In this way, and by changing the potential of the focusing cup, one may vary the brightness, cross-sectional size, and homogeneity of the beam.

Direct current is used, although the apparatus is self-rectifying, so that alternating current could be used. Ordinary alternating current is raised to the desired potential in oil-immersed transformers, rectified by means of kenotrons, and the charge stored in condensers which are connected to the cathode.

Figure 11 shows the other end of the diffraction tube,

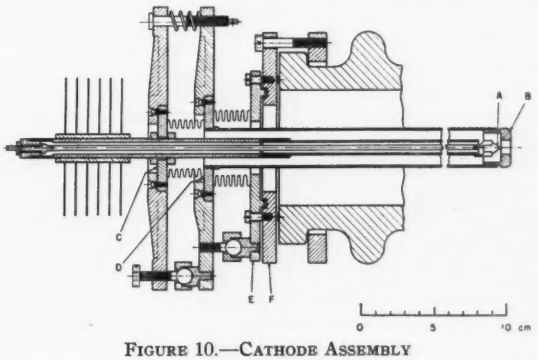

FIGURE 10.—CATHODE ASSEMBLY

which is composed largely of three-inch brass tubing. The electrons pass through the collimating tube and at *H* intersect a gas stream coming up from below. The diffracted electrons then fall upon the photographic film, which is held in the film wheel shown at the right. *D* is a steel shutter operated by a foot pedal, which is depressed at the moment of exposure. The flow of gas is caused to occur simultaneously by turning a stopcock. Exposures are generally a fraction of a second in duration.

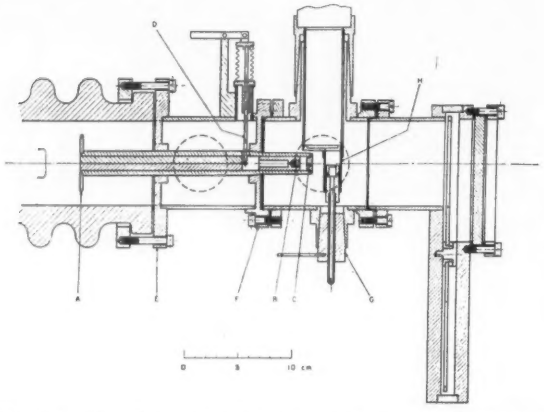

FIGURE 11.—CAMERA END OF ELECTRON-DIFFRACTION APPARATUS

The dotted circles in the figure represent openings which lead to a system of oil diffusion pumps backed by a rotary pump. Fast pumping is necessary to remove the molecules from the chamber as soon as they enter it, as otherwise they would fill the chamber, causing multiple scattering and eventually a discharge of the electron beam because of conduction of ionized particles. As soon as the gases are removed they are condensed out on surfaces cooled by liquid air.

It is necessary to know the wave length of the electrons accurately, since it enters into the formula which is used in the interpretation of the data. Determinations are made by taking pictures through very thin gold foil. The structure of the gold crystal is known, and by using the dimensions of the crystal lattice and the measurements of the photographs obtained one may determine the wave length of the electrons used to an accuracy of a fraction of one per cent.

THE STRUCTURES OF SOME MOLECULES

It may be of interest to discuss the structure of some molecules which have been investigated by the electron-diffraction method. A few compounds which are common in elementary laboratories will be chosen.

Carbon tetrachloride has been investigated with great care by a number of workers. The bonds of the carbon atom are arranged at the corners of a regular tetrahedron, as is required by stereochemical theory, and therefore make an angle of $109^1/_2°$. The distance between the nuclei of the carbon and chlorine atoms is 1.76A. Chloroform, methylene chloride, and methyl chloride have structures which are similar to that of carbon tetrachloride. Considering the great discrepancy in size, it might be thought that with substitution of chlorine atoms for hydrogen atoms the bond angles Cl—C—Cl might tend to spread out because of steric interaction. Actually this does not happen to any appreciable degree, and the reported value for the Cl—C—Cl bond angle in both chloroform and methylene chloride is 112°, less than 3° greater than the tetrahedral value. The C—Cl distance also remains constant at 1.76A.

Before the electron-diffraction experiments were made it had been thought from dipole-moment data that the Cl—C—Cl angle varied greatly in the above series. But it has been observed, in general, that the angles between two single bonds of the carbon atom are always close to $109^1/_2°$.

The structure of benzene has long been a subject of interest and controversy. It is now known that the carbon atoms are all in a plane and arranged at the corners of a regular hexagon, which is 1.39A. on edge. Its structure may be described as a resonance between several Lewis valence bond structures, the most important of which are the two familiar Kekulé structures. The C—H distance is about 1.08A.

By heating the alkali halides in a furnace to about 1200°C., the structure of the molecules in the vapor state has been studied by electron diffraction. The interatomic distances for NaCl, NaBr, and NaI are, respectively, 2.51, 2.64, and 2.90A. These distances are, on the average, 10 per cent shorter than the interatomic distances of the same compounds in crystalline form, as determined by X-ray investigations.

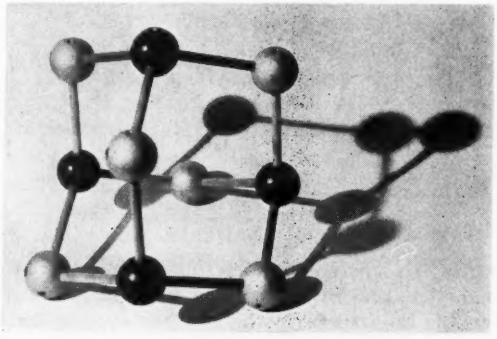

FIGURE 12.—MODEL OF As_4O_6 AND P_4O_6

In P_4 and As_4 molecules, the phosphorus and arsenic atoms preserve their trivalency by arranging themselves at the corners of tetrahedra, 2.21A. on an edge for phosphorus, 2.44A. for arsenic. In the compounds P_4O_6 and As_4O_6 the phosphorus and arsenic atoms are also arranged tetrahedrally; here, however, they are joined together by bridges of oxygen atoms (see Figure 12).

In phosphorus pentoxide, P_4O_{10}, four additional oxygen atoms are bonded to the phosphorus atoms so

that the phosphorus atoms are surrounded tetrahedrally; the P_4O_6 base is little changed.

In the linear nitrous oxide molecule, which has the formula N—N—O, the central atom is close to the point midway between the other two. The total length of the molecule, 2.32A., is in good agreement with the value of 2.31A. from infra-red data.

Carbon dioxide (*18*) is also linear; here the carbon atom is exactly at the center position. Electron diffraction and spectroscopy give the same C—O distance of 1.16 A.

The sulfur trioxide molecule is planar, with the O—S—O angle 120° and the S—O distance 1.43A. The structure theory predicts planarity of this molecule, as well as that of the nitrate and carbonate ions, which contain the same number of electrons. When, however, an unshared electron pair is present, as is the case with the trihalides of the fifth group, there is a departure from planarity, and the molecule assumes the shape of the top of an umbrella. The angles made by the halogen atoms and the central atom in the molecules of this type are about 100°.

The authors wish to thank the following for permission to reproduce illustrations: Dr. L. O. Brockway, Dr. M. E. Hufford, Dr. A. J. Stosick, Dr. G. P. Thomson, and Dr. F. R. Watson.

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A GRAPH FOR PREPARING BINARY SYSTEMS OF APPROXIMATE MOL FRACTIONS

WARD BYERLY

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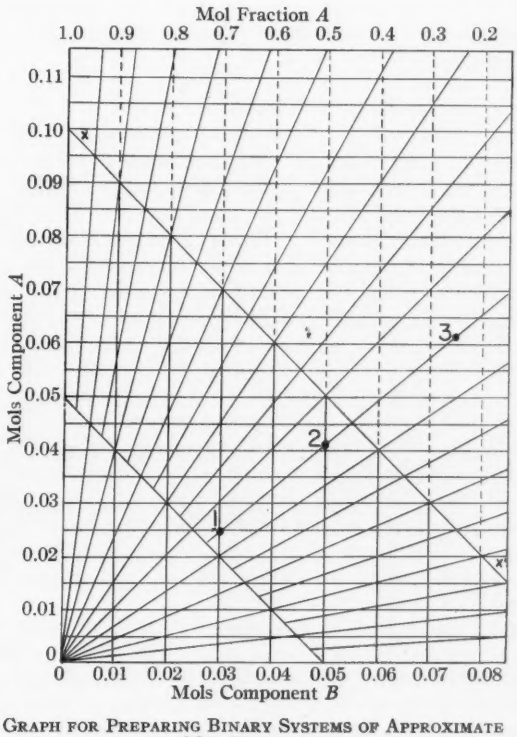
IN THE investigation of binary systems, it is often desirable to prepare a sample of a definite mol fraction. The calculations are somewhat tedious so the graph illustrated in the figure was devised. It is easily constructed and the amounts of components *A* and *B*, suitable for the capacity of the apparatus, may be determined for any mol fraction and any total amount desired.

An example will illustrate the use of the graph. Suppose a system of 0.45 mol fraction *A* is desired. Follow the dotted line from 0.45 to the intersection with the line marked *X*, *X'*. The coördinates of a line drawn from the origin through this intersection will give the relative mols of components *A* and *B* required for this mol fraction. Simple multiplication by the mol weights of *A* and *B* will give the grams of each to be weighed out.

Point 1 shows 0.025 mol *A* and 0.0305 mol *B*.
Point 2 shows 0.041 mol *A* and 0.05 mol *B*.
Point 3 shows 0.061 mol *A* and 0.075 mol *B*.

All these combinations form a system of approximately 0.45 mol fraction of component *A*.



GRAPH FOR PREPARING BINARY SYSTEMS OF APPROXIMATE MOL FRACTIONS

The Chemistry and Technology of Bread Baking

CHARLES HOFFMAN, T. R. SCHWEITZER, and GASTON DALBY

Ward Baking Company, New York City

BREAD is the oldest and most important product made from flour. Bread making dates back to that period of history when man first started to develop civilization. Bread as a food has been so important in the development of Occidental civilization that the word "bread" has become synonymous with "food." Historians believe that the earliest bread was made from stone-crushed wheat, made into a dough with water, and baked in the ashes of the campfire. Probably the Egyptians accidentally learned to use yeast as a leaven and thus produce a lighter and more palatable loaf. In the ruins of Pompeii, eighty-one loaves of bread were found; these resembled our modern bread in general appearance. Some of these loaves even had the name of the baker impressed in the crust. Thus the art of bread making is an old one and one which has steadily progressed through the ages. Today each step in the selection and preparation of the ingredients and the mixing and baking of the loaf is scientifically controlled. The baking industry today ranks as one of the greatest of the nation. The value of bread and bakery products produced in 1939 amounted to $1,371,738,372. Two hundred eighteen thousand persons were directly employed in the manufacture of bread, and they produced 300 one-pound loaves for each family of four in the United States for this same year.

DESCRIPTION OF BREAD INGREDIENTS

Flour.—The milling of flour, although an old industry, has only in recent years approached perfection under scientific control. The miller furnishes the baker with the type of flour he requires by the proper scientific selection of wheat. In general, there are two types of wheat that the miller selects for the baking industry; namely, hard and soft wheat. Flour milled from hard wheat is used for bread, while soft wheat flour is more satisfactory for cakes and crackers.

For bread making there are a number of flours in use, depending on the type of loaf required. If the entire wheat berry, for example, is ground into flour, the result is whole wheat flour from which whole wheat bread is made. The whitest type of flour is milled from the center of the wheat berry and is used for white bread, which is the predominant type eaten by the consumer. There are also flours intermediate between these two grades, somewhat dark in color, which are used for rye and graham breads.

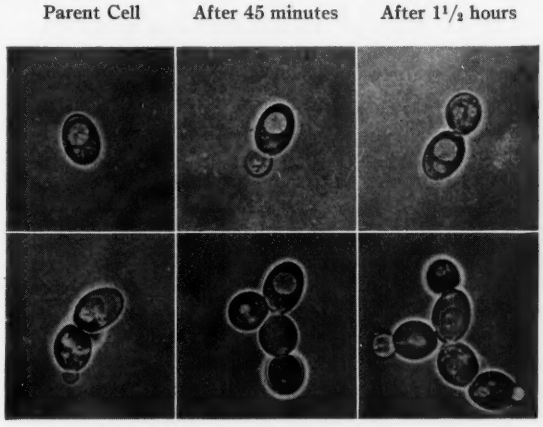
The miller and baker, using the results of chemical analyses and physical tests, judge the character and quality of flours. Flour consists of three main classes of substances: (1) starch, (2) protein, and (3) minerals. Cornstarch is a familiar example of one kind of starch. Protein is a food substance which contains nitrogen. The body uses proteins for building muscle and tissue. Common types of protein are egg whites and gelatin. Lean meats and cheese contain large quantities of protein. The minerals of wheat consist mostly of potassium and sodium phosphates with small quantities of magnesium, calcium, iron, copper, manganese, and traces of other minerals. The chemist, by a determination of the quantity of protein and minerals in flour, is able to judge the type and grade. The high-protein wheats generally command a premium, and the higher the ash of a flour, the more flour is obtained in the milling from a bushel of grain; a higher ash flour is, therefore, relatively cheaper in price. Analytical data of this nature serve as a valuable guide to the purchasing department as to the money value of a given flour.

The protein in flour is very important to the manufacture of bread since it forms the framework for the loaf and gives it a light, porous structure. The action of yeast generates gas (carbon dioxide) in the dough. The protein forms a glutenous mass much like a rubber tissue which retains the carbon dioxide and thus permits the dough to rise and then expand during baking.

Milk.—Everyone knows the nutritional value of milk and its place in the diet. During recent years the baking industry has increased steadily the quantity of milk used in the manufacture of wheat bread. Milk adds to the palatability and to some extent retards staling of the loaf. Milk is a perishable food, and when large quantities are used, as in baking, special precautions must be taken to insure that the milk is clean and pure. If part of the water is removed, condensed milk results. This product has good keeping qualities, and serves excellently in the bakery. If the process of removal of natural water of milk is taken to essential completion, the result is dry milk. Dry milk, or milk powder, is as easily handled as flour or sugar, does not spoil, and does not require refrigeration. Because of its convenience most bakeries now use milk powder. It contains the valuable protein, minerals, and vitamins of natural milk, and the removal of water does not affect its nutritional value.

Yeast.—Yeast is a microscopic one-celled plant which has the ability to utilize sugar and break it down into two main products, alcohol and carbon dioxide gas. The carbon dioxide gas so produced is the actual leavening agent in bread. Yeast produces the carbon dioxide in bread dough, whereas in cake dough the carbon dioxide is produced by baking powder. Baking powder consists of a mixture of sodium bicarbonate and an acid such as tartaric acid. In the cake dough the acid releases the carbon dioxide from the sodium bicarbonate. Present-day yeast manufacturers take great care to insure the purity of their product, and

deliver it fresh to the baker every day. Bread dough, because of the yeast added, contains large numbers of microscopic yeast cells; in fact, the dough of a one-pound loaf of bread contains 50,000,000,000 live yeast cells, which, however, are killed by baking. A yeast cell is so small that 5000 are required when laid side by side to make an inch. A cubic inch of compressed yeast will contain 125,000,000,000 cells, each a separate plant.



Courtesy of The Fleischmann Laboratories

PHOTOMICROGRAPHS OF YEAST CELLS SHOWING THE DEVELOPMENT OF A GROUP OF CELLS FROM ONE PARENT CELL

Yeast Nutrients.—The yeast plant requires food on which to live. The bread dough furnishes all the sugar necessary for yeast growth and the production of carbon dioxide gas. Research has shown, however, that the dough does not contain the types or quantity of mineral salts required for optimum yeast growth. Fifty billion cells growing in the dough for a one-pound loaf need considerable mineral nutrients. If small quantities of mineral salts containing nitrogen and calcium are added to the dough, much better growth of yeast and consequently a better dough development are obtained. These minerals have been proved so important in yeast growth that yeast manufacturers now use these salts to aid in the production of yeast for bakers.

Mineral Salts.—Common salt (sodium chloride) is used in the manufacture of bread to give flavor and taste to the finished loaf, to regulate the action of the yeast, and also to give stability to the dough. Salt manufacturers and baking laboratories test the salt to be sure of its chemical purity.

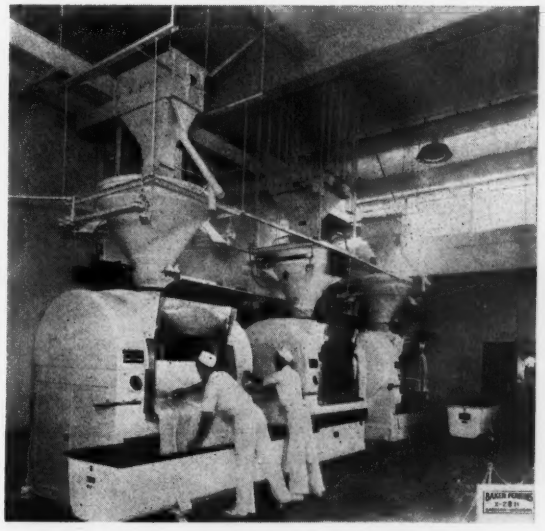
Shortening.—Various types of shortening are used in bread. The two most usual types are lard and vegetable shortening prepared from cottonseed oil. Other shortenings are available for use in bread; these include oleo oil, soya bean oil, and various coconut and palm oils. It makes no essential difference in the finished bread what type of shortening is used, provided the shortening itself is of good quality. If the price of lard is lower than that of vegetable shortening, lard is used; and if vegetable shortening is lower in price than lard, the reverse is true. The manufacturers of shortening test their products for purity and for keeping quality.

Sugar.—Various types of sugar are available for use in bread. These include cane sugar, beet sugar, sugar syrups, corn sugar and syrup, molasses, and honey.

THE MANUFACTURE OF BREAD

Making bread in the home has always been considered somewhat of a chore, but even so it is seldom looked upon as a complicated process. The manufacture of bread on a large scale is a complex procedure, and every step is carefully controlled in order to insure good and uniform quality.

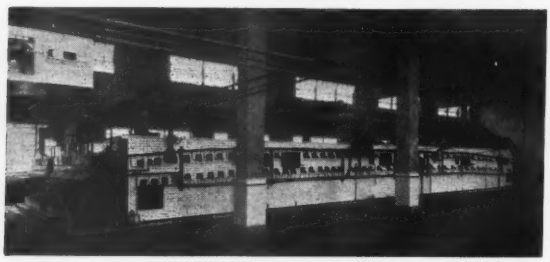
In general there are two processes for the manufacture of bread. One, called the straight dough process, is used only to a small extent. It consists of mixing all ingredients together at one time. The second method, called the sponge-dough process, consists in the mixing of the sponge and allowing it to ferment. The only ingredients in the sponge are flour (about 60 per cent of the total flour to be used in the batch), the yeast, yeast nutrients, and water. After the sponge has fermented, the remainder of the flour, shortening, milk solids, salt, and sugar are added; the dough is mixed and again allowed to ferment. The sponge-dough process is longer and requires two mixings, hence more machinery and labor, but is more suitable for the modern type of bread than the straight dough process.



DOUGH KNEADING MACHINES (MIXERS)
Delivering 1000 pounds of mixed dough into a trough

The steps of the sponge-dough process follow. The time intervals given are for the handling of 1000 pounds of dough. All of the dry ingredients are sifted just before using as an extra check on purity. The sponge, consisting of flour, yeast, yeast nutrients, and water, is mixed for six to seven minutes. It is placed

in a dough trough and allowed to ferment for four and a half hours. The sponge is returned to the mixer, the additional ingredients are added, and mixing is carried on for ten minutes. The batch of dough is placed in the trough and allowed to ferment for half an hour. After this last period of fermentation, the dough is ready to be taken to the divider. This machine divides the dough into pieces, each of which when baked will give a loaf of the desired weight. Fifteen minutes are required for 1000 pounds of dough to pass through the divider. Each individual piece of dough then goes through the rounder, which shapes the dough into a smooth ball. After rounding, the dough is allowed to rest for about ten minutes in order to give it time to recover and expand in preparation for the next stage of the process. Each individual piece of dough then goes through the molder which forms it into the shape of a loaf. Then it is placed in the baking pans. Molding and panning together require about ten minutes for the 1000-pound batch. The pans containing the pieces of dough are placed in a warm, humid, proofing room and allowed to rise for one hour. At the end of the proofing period, the dough almost fills the pan. The next step is the actual baking in long continuous baking ovens, a process which requires 30 to 35 minutes. The pans with the dough enter the oven at one end and emerge at the other with the golden brown loaves all of uniform bake and crust color. About one and one-half hours are required for cooling. The bread is then sliced and wrapped in wax paper or cellophane, packed in delivery boxes, and distributed to the grocery trade.



TRAVELING OVEN

This oven bakes 5000 loaves per hour. The bread travels slowly from the time it enters the oven until it emerges, covering a distance of 100 feet

A period of nine hours is required, therefore, for the complete preparation of a commercial batch of bread.

THE BACTERIOLOGY OF BREAD

In addition to staling, bread, like many other foods, is subject to spoilage. Two troublesome types of spoilage encountered are "ropy" bread and "moldy" bread.

"Ropy" bread is caused by harmless bacteria, although of a type which produces disagreeable odors. These make the product unfit for human consumption. The bacteria are present in the ingredients from which the bread is made, and are able to live through the baking process and grow in the loaf while in the grocery store or in the home. The name "ropy" bread was given to this condition because after the bacteria grow in the loaf, the loaf becomes sticky and stringy and may be stretched out somewhat like chewing gum. Thus it was said that the bread contained "strings" or "rope." This condition may be prevented by proper selection of flour, yeast, and other ingredients used in the bakery. Tests made on the ingredients will determine whether or not significant quantities of the bacteria causing "rope" are present. Those ingredients which contain the bacteria are of course rejected.

Mold growth may be seen in the home on the tops of jelly jars and on cheese, and quite frequently on the bread in the bread box of the kitchen. Mold is a low form of plant life. Different varieties are of various colors; therefore one may see black, green, white, yellow, and red mold growths. Mold will grow on any food product containing sufficient moisture, and bread, being moist, is ideal. The slicing and wrapping of bread has added to the seriousness of the mold problem for the commercial baker.

A great deal of study has been devoted to the problem of preventing bread from becoming moldy. Mold spores or "seeds" are universally present in the air, and it is impossible to prevent these seeds from settling on the loaf while it is cooling after being baked. Research has shown, however, that substances like calcium propionate, which occur naturally in many types of food products such as cheese, sour milk, and butter, have the property of delaying the growth of mold. Calcium propionate is now available as a bread ingredient, and its use increases the lime content of the loaf, adding to the nutritional value of the bread.

THE IMPORTANCE OF BREAD AS A FOOD

Bread and other bakery products are the most universally used of all foods. The common types of bread consumed in the United States are white, graham, rye, and whole wheat. A graham loaf is often made from a mixture of white and whole wheat flour. A great variety of rolls, buns, coffee cakes, and breakfast pastries is manufactured and consumed. Bread may be eaten in many forms. It is probably most commonly served sliced directly from the loaf. It can be served in the form of sandwiches, toast, and French toast. Bread is also used in the preparation of other foods such as stuffing for roast chicken or turkey, in meat loaves, in bread puddings, and for breaded chops, fish, and oysters. Since bread is so important in the feeding of the nation, the bakers of the land have endeavored to place in the hands of the consumer the best possible product. Bread at the present time is without doubt the safest and most sanitary food product available to the public. It is usually marketed in a waxed, moisture-proof paper insuring cleanliness and freshness for the consumer. Within modern times no infectious disease has ever been traced to bread.

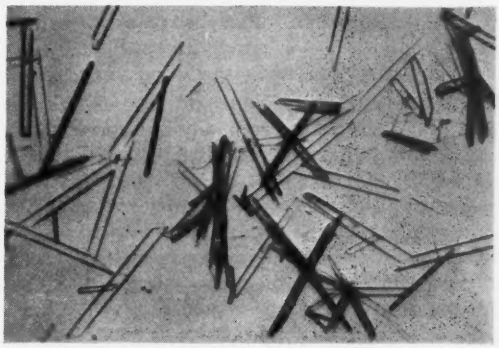
Bread contains five main types of food essentials: (1) carbohydrates, (2) proteins, (3) fats, (4) minerals,

and (5) vitamins. The carbohydrates of bread, sugar and starch, are energy-furnishing materials and serve the energy requirements of the body in the same manner as gasoline furnishes the energy requirement of an automobile. The proteins of bread are muscle and tissue-building substances. The minerals of bread play an important part in the growth and maintenance of the human body. Calcium builds bones and teeth and keeps them in repair. The phosphates are valuable in association with calcium for the same purpose. The iron, copper, and manganese aid in the production of the hemoglobin of the blood. Since such a large quantity of bread and bakery products is consumed, the vitamins in bread are especially important in nutrition. A person may have all the sugar, fat, protein, and minerals that he needs, but yet be undernourished unless he has vitamins in his diet. Wheat is perhaps nature's most important storehouse of the B vitamins. Vitamin B_1 promotes growth, aids digestion, and is essential for proper nerve function. Vitamin B_2 (riboflavin), among many other important functions, aids in maintaining the eyes in normal condition. Nicotinic acid, an important member of the B family of vitamins, prevents the deficiency disease, pellagra. There are also a number of other members of the B complex present in wheat which have not been fully studied in their relation to human nutrition.

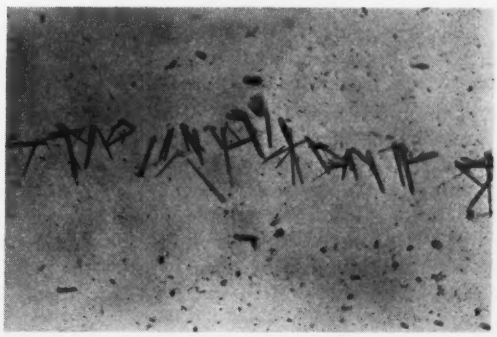
From the very beginnings of recorded history man has preferred white bread over the darker types of bread. In Greek mythology, for example, it was explained that white bread was suitable for the gods, whereas the common mortal had to subsist on dark bread. The milling industry, due to public demand, has, over the years, continued to produce white flour. High-quality white flour is derived chiefly from that portion of the wheat berry which contains the lowest concentration of the vitamins of the B family and the mineral content of the wheat. As the science of nutrition developed, authorities began to realize that the public was not getting a sufficient quantity of vitamins and minerals for optimum health. The United States Department of Agriculture in a recent dietary survey estimated that one-third of the entire population are receiving diets which, according to modern standards of nutrition, are definitely inadequate. This inadequacy does not refer to a lack of calories supplied by carbohydrates, proteins, and fats, but means that they are not getting the proper vitamins and minerals.

ENRICHED BREAD

The Committee on Food and Nutrition of the National Research Council, recognizing that this problem exists, has undertaken in coöperation with the millers, bakers, and various departments of the national government a program of bread enrichment. The program of producing a white loaf of bread which shall have the essential vitamins and minerals in amounts equivalent to whole wheat is now under way. This program will place white bread in a preferred nutritional class with whole wheat bread. Only a small percentage of people like whole wheat bread as a steady diet, and much prefer white bread for its appetizing flavor. Also for many people white bread is more digestible than whole wheat bread. For these reasons it was decided to enrich white bread rather than attempt to ask the public to eat whole wheat



VITAMIN B_1
(Thiamin Hydrochloride)



VITAMIN B_2
(Riboflavin)

VITAMIN P-P
(Nicotinic Acid)

Photomicrographs courtesy of Merck and Company

PHOTOMICROGRAPHS OF PURE VITAMIN CRYSTALS
Three of the important vitamins to be added to enriched bread

bread. Two slices of enriched bread eaten three times a day will supply a good portion of the daily requirement of the essential vitamins and minerals.

THE DUTIES OF THE BAKING-LABORATORY CHEMIST

The duties of the baking-laboratory chemist may be discussed under three main divisions; first, ingredient control; second, analysis of finished product; and third, research or the study of how to improve the quality of the raw materials and the finished product.

The number of ingredients and raw materials purchased by a large baking company is surprisingly large. Flour, yeast, salt, sugar, shortening, yeast nutrients, mold inhibitors, milk, eggs, butter, and flavoring materials must all be analyzed for purity and quality, and check samples must be taken periodically to insure the uniform quality of the ingredient. Besides those actually used in the manufacture of bread, many other products must be purchased. The trucks in which the bread is delivered must have gasoline and lubricating oil, and cleaners must be purchased to wash the lacquered surfaces of the trucks. Cleaners for pans, walls and floors, and hand soaps for the employees must be checked in the laboratory for quality. The coal, gas, and fuel oils require laboratory analysis. The quality and type of the water supply must be known, and this of course requires water analyses.

It is often desirable to analyze the finished product in case any question arises as to the effect on quality of the variation in quantity of any of the ingredients. Also, the bread must be analyzed in order to furnish information to hospitals, dietitians, and other interested persons concerning its actual food value. The hospital dietitian, for example, may want to know the percentage of carbohydrate, protein, and fat in the bread; the number of calories per slice; the calcium and iron content; and the value of the bread with respect to the various vitamins.

The food chemist is constantly striving to improve the quality both of the ingredients that go into the bread and the bread itself. For example, it is now evident that some of the ingredients used in bread at times contain the bacteria that cause "ropy" bread. Continuous bacteriological tests on every shipment of materials such as yeast, malt, and milk for a long period of time have shown the unsuspected source of infection. This research project led to the elimination of the bacteria from the dough batch. Research on methods of analysis is important, and as improvements in the product occur new methods are needed. Years ago not much milk was used in bread, but now almost all white bread contains milk. This fact made necessary the development of a reliable method for the chemical determination of milk in bread.

The discovery of the value of calcium propionate as a "rope" and mold inhibitor in bread was the result of a long-continued research program. The baking industry for many years had used substances such as vinegar and calcium acid phosphate to combat mold and "rope" with some degree of success, but did not completely solve the problem. It was discovered that propionate salts present in butter, cheese, sour milk, and other fermented products were excellent mold inhibitors. This fact was only the first part of the research project. The second part was to find out how to use it in bread, and then the best method for use in the commercial bakery.

Developments in the baking industry, such as the program of bread enrichment with vitamins and minerals, bring up problems which must be solved and controlled in the food laboratory.

● Mass spectrographs, until this year little more than instruments of scientific research, may find widespread application in process control of petroleum refining, according to a dozen leading petroleum engineers who recently examined a newly developed mobile unit at the Westinghouse Research Laboratories, East Pittsburgh, Pennsylvania.

Mounted on a small truck, the mass spectrograph could be wheeled from place to place in the refinery, if mobility were necessary, to give quantitative analyses of gases tapped from fractionating towers at various stages of the process. If the constituents of the gas are known in advance, as they are in refining, the instrument "sorts" the different molecules according to their "weight" or mass, and can determine the relative quantities of the constituent gases with an accuracy of one part in 100,000.

Another suggested use for it in the petroleum industry is in prospecting for oil. Gases are extracted from samples of earth and analyzed for traces of certain telltale hydrocarbons that indicate the presence of oil-bearing strata beneath the surface.

● America's Modern Plastic Exposition, composed almost entirely of winners in the recent Modern Plastics Competition, is appearing in large department stores and civic centers from coast to coast.

It is the first exhibit of its kind ever to be assembled and brought directly to consumers, accomplishing the twofold purpose of stripping plastics of technical bugaboos laymen do not understand and educating the sales personnel of the various stores as to just what plastics are. Actual molding of plastics under laboratory conditions is performed as part of the exhibit, demonstrating in miniature just how the many available plastics are being molded on a larger scale by the plastics industry.

An American flag made of plastic materials in brilliant colors dominates the section of the exhibit devoted to plastics in National Defense. This division spotlights outstanding applications of various plastics in airplanes, tanks, guns, gas masks, flame-throwers, and the like, and brings home the vital role they are playing in our national security.

Industry's Challenge to Chemical Education

FORREST A. ANDERSON

Wilkens-Anderson Company, Chicago, Illinois

THE basis for Industry's challenge to chemical education is the necessity for a clearer recognition in the college that training may proceed simultaneously at several different levels. Chemists need not be turned out all cut to one pattern. Analysts, technicians, investigators, and research experts—all are necessary and can find their places in the industry. The greatest efficiency will result not from trying to outline one type of training for all but from adapting it to meet the needs of industry and the capacity of the student.

Education might be defined as the enrichment of the mind and the enlargement of vision. It is three-dimensional. It should give height, depth, and breadth: height of one's standard of accomplishment, depth of insight, and breadth of view and understanding. It also gives to the mind a better conception of vision and power. Training might be said to make the mind a more effective tool by giving it a keener edge for cutting and the proper shape and temper for the material upon which it is to work.

A friend of mine can write entertainingly and talk on all manner of subjects, but he has never been able to hold a good paying job. He has education but not training. It is just as common to find men who are excellent technicians but poor companions, either on the job or on a fishing trip. All of us who are interested in a modern system of education believe that those who teach and train must join in the common enterprise of helping the student achieve his highest and richest self-development.

If you hope to choose chemistry as a profession it may be because a teacher encouraged you in experimental research, probably in your first course in general chemistry. The first function of general chemistry should be to arouse curiosity; second comes the joy of fact finding and the acquisition of knowledge; and third, the sense of accomplishment which rewards the carrying out of a simple research. What is the correct balance of curiosity, knowledge, and judgment in a course in chemistry planned for the various mental levels?

The courses in a large majority of the colleges today are gaited for the weakling. A good proportion of the time of the faculty is spent cramming a stereotyped factual education down the throats of hundreds of students who are in our state schools simply because the social and industrial situation drives them there, or it is the smart thing to do.

Lack of guidance and a very narrow conception by many chemistry teachers of the larger obligation of the school to the student in our American society, and a false idea of standards, prevent the making of well-trained mechanics and electrical engineers in place of some of the poor chemists and engineers who are graduated. This system penalizes the good, capable student, who founders and loafs while the teacher's efforts are spent on the weakling in order to get him over the intellectual line.

Some of our colleges are trying to teach men in the various intellectual levels a tailor-made brand of chemistry to fit them for the type of work they are *able* to do. The organization of the courses in elementary chemistry at Princeton University is a good example of this.

Four courses are offered in which, respectively, the three elements of curiosity, knowledge, and judgment are involved as follows:

	Course			
	1	*2*	*3*	*4*
Curiosity	*****	***	**	*
Knowledge	*	***	****	****
Judgment	***	***	****	********

Course 1 is for those who have never had any formal scientific experience, and will perhaps have no more beyond this. It is a thorough course in general chemistry, locally known as "Housemaids' Chemistry." Students are taken into the laboratory only a half-dozen times during the year. Curiosity must be greatly stimulated by lecture demonstrations, field trips, etc. Facts are unimportant; principles are vital. Thus, when simple organic chemistry is reached, neither a panorama of organic compounds nor a parade of organic formulas is offered. Instead, the proof of structure of some simple compounds and the methods of synthesizing organic molecules are presented.

Course 2 is a more conventional elementary course for beginners who have had no preparation. Curiosity must again be aroused, for many students have never before carried out any experiments. Facts in this course are vital as working tools. As much critical judgment is cultivated as time allows.

It is unnecessary to arouse curiosity in courses 3 and 4. These students are scientists at heart. Eleven-fifteenths of them have already signified their intention of becoming chemists, doctors, or engineers. They are trained to exercise critical judgment to the utmost. Course 4 is especially interesting, constituting the brightest men in the freshman class. Curiosity and enthusiasm run high; these students are lavish in their criticisms. Here the task of the teacher is to restrain their critical judgment until their fund of knowledge becomes extensive. They must build a firm foundation. They are stimulated to original thinking, to extensive correlation of data, to a broad understanding of the interrelationships between the different sciences.

Now let us briefly review some of the kinds of chemical work for which special training is necessary.

CHEMICAL TECHNICIANS

A chemical technician is generally a person who runs routine analyses, of which nearly every industry has a host. In the laboratory of a steel plant, where hundreds of determinations of phosphorus, alumina, silica, and sulfur are run, high-school boys are often employed to perform this punch-press type of work. Undoubtedly college-trained men would be more valuable, but might not be content to perform this kind of work indefinitely. They have accepted such a position only as a steppingstone until a better opportunity presents itself. Other industries have similar routines every day. Mechanics who are handy in skills such as glass blowing, wood and brass turning, taking charge of chemical stores and supplies, etc., are always in demand.

OPPORTUNITIES FOR WOMEN

Women in chemistry have always been a problem. With few exceptions they have not been found well adapted to positions in industrial laboratories. But there are opportunities for which a background of chemical training can fit them. These include positions as laboratory technicians, routine analysts, science librarians, patent researchers, and technical secretaries.

In planning educational programs for women chemists certain points should be kept in mind: The program should be definite and not haphazard; training should be begun in the freshman year with as early specialization as possible; contacts should be made and maintained with firms using women chemists.

ELECTRICAL SKILLS—ELECTRONICS

Instruments constructed with radio tubes, photocells, electronic valves, etc., are coming into wide use in industry today. Many a boy, from a humble beginning as a short-wave amateur, has paved a way for a life's vocation in the field of electronics. Most of the universities and many of the smaller colleges are combining the practical application of these useful instruments into a course in instrumentation. X-ray investigation of steels and alloys, pH electrometers, hydrogen ion recorders, photelometers, and spectrophotometers are but a few of the many useful tools.

Instrumentation is proceeding at a great rate. Visual colorimeters, for example, have been almost entirely replaced in modern laboratories by photoelectric apparatus. Investigation of vitamins with spectrophotometers is the latest order of the day.

There is little evidence to show that the mind of modern man is superior to that of the ancients. The early philosophers disdained experiment and even common observation, if the results were contrary to apparent logic. Devising new precision instruments is as important as the discovery of a fundamental truth. On the average staff of instrument makers will be found Ph.D.'s as well as skilled mechanics. The microbalances, fluorophotometers, and X-ray diffraction instruments of the next ten years will depend largely on the quality, versatility, and common sense of the men turned out by the colleges and universities.

Research men are rapidly being classified in the larger laboratories of the United States. The value of specialized experts versed in the use of the ultracentrifuge, electron microscope, and other instruments is being recognized.

SPECIAL INVESTIGATORS

Criminal detection and other types of chemical forensics present a broad field of possibilities. A reading knowledge of modern languages is invaluable for this kind of work, which has a great future. An open mind is necessary and this type of research is quite different in its nature from the usual sort in a chemical laboratory. Many men who have taken up this field of work have found a minor in bacteriology very useful.

SALES

A successful man in any commercial enterprise is a gentleman skilled in the arts he is trying to practice. The day of the domineering bully is past in the industrial world and today success requires that a man be honest, straightforward, and a square shooter—one who also commands the respect of his associates and everyone with whom he comes in contact. In other words, he must be practiced in the art of rubbing shoulders with all kinds of men. A technical education if obtained under the right auspices should teach a man to observe keenly, draw logical conclusions based on the perceptions of the five senses, and banish the superstitions of business. Conclusions then become the basis of sound reasoning based on facts, not hunches.

Success in sales management in the future will be more dependent upon sound technical education than in the past. Social adaptability is as necessary in a sales-service manager as is a broad basis of sound chemical education. He must know more about the technical application of the new instruments to the problems of his customers than the customer himself. "High-pressure salesmanship" then becomes more an expression of skilled technic than a barrage of clever words. The customer, often the superintendent, is not a college man. He has learned the business from the ground up, the hard way. Usually he expects the worst from a salesman and is pleasantly surprised when a technical adviser gives real information based on sound scientific observation. Of such stuff is success made in the selling profession. A salesman may come from the laboratories, but the process is hardly ever reversible.

CONCLUSION

The changing world demands that the liberal arts colleges of tomorrow recognize and meet the hundred and one new challenges. From these institutions of learning many of America's best scientists receive their primary training. And what is more to the point, the

writer believes an educational contrast is presented which may supply a perspective of practices and standards as measured by those prevalent in other countries.

Phase Rule Experiments with Organic Compounds

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HETEROGENEOUS equilibrium is one of the more important topics covered in all courses in physical chemistry and the most important subtopic in this field is without doubt the study of the principles and applications of the phase rule. It is customary

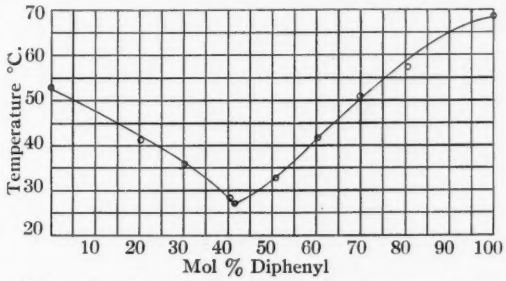

FIGURE 1.—SYSTEM: DIPHENYL–*p*-DICHLOROBENZENE

to include in the laboratory of most physical chemistry courses an experiment on the phase rule. This is usually the determination of the temperature–composition diagram of some metallic system by a study of cooling curves of different mixtures of the metallic components. The systems most often recommended employ metallic components, and, though they seldom tend to supercool, suffer from several serious difficulties. Fairly high temperatures must be employed

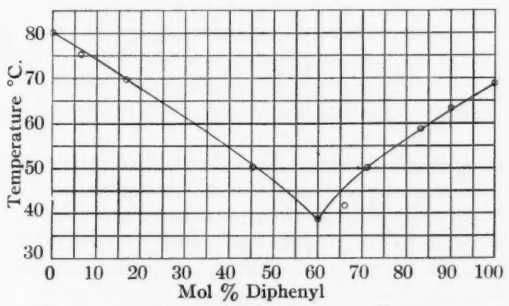

FIGURE 2.—SYSTEM: NAPHTHALENE–DIPHENYL

and oxidation is difficult to prevent. The number of metals melting within the temperature range of most laboratory apparatus is limited, thus giving no great variety of systems or types of systems from which to choose suitable class illustrations.

On the other hand, most organic solids melt in the temperature range from room temperature to 200°C. which is the most desirable laboratory range. When one first considers the possible number of binary organic systems, the number available seems limitless. In practice, however, there are certain factors which limit the use of many organic compounds for this type of work. The compounds must be inexpensive, readily available, easily purified, non-corrosive, stable in air and upon heating, and of such physical form that they can be easily weighed and handled. Needless to say, no chemical reaction should take place between the components in any given mixture.

An extensive bibliography of organic systems and their phase diagrams is given by Timmermans (*1*)

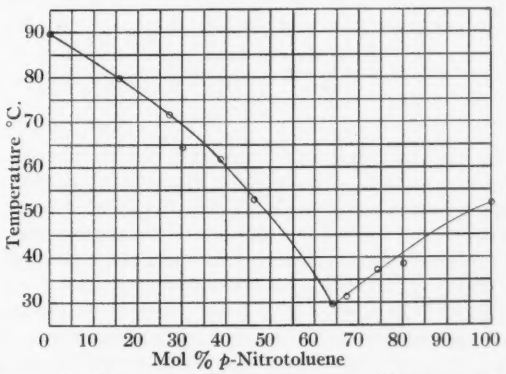

FIGURE 3.—SYSTEM: *m*-DINITROBENZENE–*p*-NITROTOLUENE

and the standard tables (*2*). Also a number of authors (*3*) have suggested various organic systems suitable for this purpose.

In the present investigation a study has been made of a number of systems to determine those best adapted for student experiments in physical chemistry. All the systems recommended by others have been tried and a number of new systems were examined also.

EXPERIMENTAL DETAILS

The method of experimentation was simplified as much as possible. In every case the mixtures were prepared by melting together weighed pellets of the components. This was done at the lowest possible temperature in a wax bath and various compositions

were obtained by adding further weighed pellets of either component. The apparatus used was simply a six-inch pyrex test tube provided with a thermometer of suitable range and a loop stirrer made of No. 16 B and S gage nickel wire. It was found that the wax coating from the melting bath provided suitable insulation to slow the cooling in air down to a suitable rate.

To avoid supercooling the mixtures were stirred and sometimes small crystals of the solid mixture, previously removed, were introduced just below the melting point. It was found unnecessary to plot cooling curves. The separation temperature was easily obtained from the maximum reached after supercooling. When the final eutectic was below room temperature, the tubes had to be immersed in cold water to reach the solidification temperature.

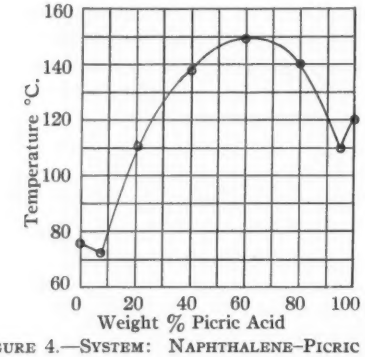

FIGURE 4.—SYSTEM: NAPHTHALENE–PICRIC ACID

In the examination of mixtures which form solid solutions, it was necessary to modify the procedure. Two schemes were tried. First that labeled "end of melting" or "endpoint" represents the temperature of the mixture when the last portion of paste changes to solid crystals. The other method requires a rapid cooling of the melt in a 17.5-cm. pyrex test tube under the cold water tap. The liquid solidifies at once and all is of the same composition. Before cooling this a thermometer is centered in the tube and thus is frozen into the solid. This tube is then placed in a beaker of water which is slowly heated, the thermometer inside registering a difference of not over one-half a degree from that shown by a similar thermometer placed in the water just outside the tube. The temperatures of the two are averaged and recorded as the "thaw point" as the first crystals of solid change to liquid. Mixtures were made up to consist of definite weight per cent of one component, and the first separation temperature was found in the usual way of maximum rise after supercooling.

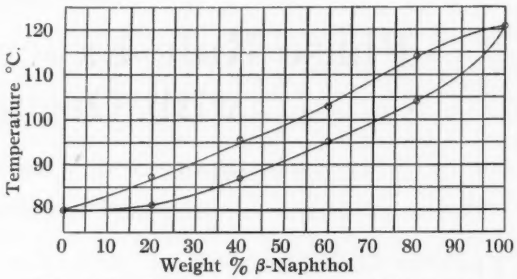

FIGURE 5.—SYSTEM: NAPHTHALENE–β-NAPHTHOL

RESULTS

Of the systems investigated, those which were found to be satisfactory are given in Table 1.

TABLE 1

ORGANIC SYSTEMS SUITABLE FOR PHASE RULE STUDIES

System
p-Dichlorobenzene–Diphenyl
Naphthalene –Diphenyl
m-Dinitrobenzene –*p*-Nitrotoluene
Naphthalene –Picric acid*
Naphthalene –β-Naphthol
Naphthalene –β-Naphthylamine

* Although picric acid is explosive, no difficulty was encountered as long as the temperature was kept below 250°C.

To illustrate the nature of these systems their phase diagrams are shown in Figures 1 to 6. These diagrams were constructed from data actually obtained in the laboratory.

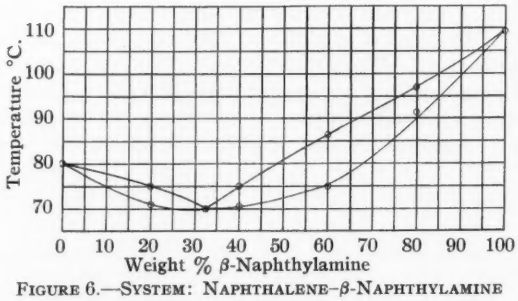

FIGURE 6.—SYSTEM: NAPHTHALENE–β-NAPHTHYLAMINE

As a laboratory experiment the student can complete one system and perhaps two in the usual laboratory period if supplied with the pure components.

We wish to express our thanks to Professor Harold A. Iddles for his help in selecting suitable organic substances for trial.

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(1) TIMMERMANS, "Les solutions concentrées," Maussent Co., Paris, **1936**.
(2) (*a*) "International critical tables," McGraw-Hill Book Co., Inc., New York City, **1928**, Vol. IV.
(*b*) LANDOLT, BÖRNSTEIN, ROTH, AND SCHEEL, "Physikalisch-chemische Tabellen," Julius Springer, Berlin, (5), **1923**.
(3) (*a*) FINDLAY, "Practical physical chemistry," Longmans, Green and Co., Inc., New York City, (6), **1935**, p. 296.
(*b*) VERNON, J. CHEM. EDUC., **15**, 88 (1938).
(*c*) BRIERS, *School Sci. Rev.*, **17**, 461 (1936).

How Do Chemistry Teachers Improve Their Teaching?[1]

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RUFUS D. REED *New Jersey State Teachers College, Montclair, New Jersey*

THIS paper will deal with the teaching of chemistry as a scientific problem. For the most part, it will be limited to discussion of the first-year college course in chemistry.

The problem of teaching chemistry requires, as do all scientific problems, clear and careful statement, framing of hypotheses, observation, measurement, and, finally, the most cautious generalization with further scientific checks. Furthermore, it requires a conviction that questioning of current practices is useful. A good many chemistry teachers have such a conviction. This is indicated by the results of a study made by the American Association for the Advancement of Science Committee on the Improvement of Science Instruction for Purposes of General Education.[2] Answers were given to a questionnaire by representatives of chemistry departments in 211 colleges and universities. About two-thirds of this group believe that the method or content of the conventional introductory course in chemistry is not satisfactory for the student who is not specializing in chemistry. Over half of the departments report that the content and program of instruction has been considerably modified within the framework of the old course. In a few cases the department has replaced the old course with a survey course in the physical sciences. A third of the departments have introduced new freshman courses in addition to the regular introductory course.

A number of the larger universities, which have large freshman enrolments in chemistry, are experimenting in a thoroughly scientific way with the first-year chemistry course. With large enough enrolments to permit the offering of several different courses, they are able to compare the results of various ways of teaching. The reports of these experiments, published in the JOURNAL OF CHEMICAL EDUCATION and elsewhere, are building up a substantial body of fact about chemistry teaching.

However, making an exception of these admirable studies and of the brilliant work of a few outstanding teachers, it must be said that much of the experimentation of the past ten or fifteen years has been rather aimless. There are three reasons for this.

One reason is that there is no clear agreement or understanding among college teachers concerning the aims of college education. There will usually be vast differences in the aims of people in the various colleges on a single university campus. The college of agriculture may want one kind of outcome from the chemistry course, while the college of engineering wants another, the college of commerce still another, and the college of liberal arts may disagree with all the other colleges, as well as within itself. There is nothing inherently bad about the presence of diverse educational aims in different parts of a university, but, unless the aims are clearly stated and understood, a department such as chemistry, which attempts to serve a number of colleges within the university, cannot be very sure about what it is doing.

Another reason is that chemistry teachers are not clear in their own minds about the place of science (and especially chemistry) in general education at the college level. Since most of the liberal arts students taking chemistry will not specialize in it and will not use it as a vocational tool, chemistry is for them a part of general education. In the questionnaire referred to above, three-fourths of the college representatives indicated that there was need for clarification of the place of science in general education, for teachers of chemistry.

A third reason for the aimlessness of much of the recent experimentation is that chemistry teachers have not treated their teaching problem as a scientific one, deserving the same intelligence and industry, scientific method, and attitude that they devote to research in chemistry.

But, fortunately, the situation is changing rapidly. Chemists are beginning in large numbers to study the problem of teaching science as a scientific problem. Here is the thesis of this paper. Chemists improve their teaching by making a scientific study of the problem of teaching.

The problem of teaching chemistry can be stated as a scientific one as follows. First, what do we hope to accomplish through our teaching—what are our objectives? Second, what kinds of experience will probably help students to achieve these objectives? What kinds of reading, observation, laboratory work, discussion, work on problems, etc., will probably result in the outcomes we expect from the study of chemistry? Third, what kinds of student behavior will we accept as good scientific evidence that we are accomplishing what we set out to achieve? For example, do we want the following kinds of behavior: ability to apply chemical principles in new situations, ability to draw inferences from chemical data, knowledge of the meanings of certain terms, solutions of certain problems, answers to certain test questions, ability to set up apparatus to

[1] Presented before the Division of Chemical Education at the 101st meeting of the A. C. S., St. Louis, Missouri, April 9, 1941, and revised in July, 1941.

[2] TAYLOR, HEIL, AND SCHAEFER, "Chemistry instruction for purposes of general education," J. CHEM. EDUC., **18**, 10–14 (Jan., 1941).

prepare a certain gas, ability to design a procedure for detecting a certain metal in an unknown substance, etc.? Finally, what are the most practicable and valid methods of observing and recording the kinds of student behavior in which we are interested? For example, would we be satisfied with: a test of the essay type, observing and rating students in the laboratory, a term paper, a paper-and-pencil test of the objective type, etc.?

In work of this kind, the statement of objectives of teaching is fundamental. The questionnaire of the A. A. A. S. Committee asked the question, "What do you believe are the most significant contributions which a study of chemistry should make for those students who are not to specialize in chemistry?" Respondents chose the following as the three most important contributions, in the order named:

1. Develop the ability to do critical thinking.
2. Make students familiar with the facts, principles, and concepts of chemistry.
3. Show how the discoveries of science have contributed to the solution of some problems of living and have created others.

Inspection of these contributions (or objectives) of chemistry teaching will probably suggest to the teacher that different content and perhaps different methods will have to be used to achieve the different objectives. It is rather clearly apparent that the second and third objectives require different kinds of teaching. The first objective might be expected to result from teaching directed at the achievement of the second one. Many teachers assume this to be true. A few people, not so sure of this, have set out to test the hypothesis that ability to do critical thinking results from teaching that is aimed to make students familiar with facts, principles, and concepts of science. They have designed tests of ability to do critical thinking *on scientific subjects* and compared the performance of students on these tests with their performance on tests of knowledge of facts, principles, and terminology of science. At the Ohio State University and at the University of Minnesota, where this work has been carried on, very little relation was found between students' achievement of these two hoped-for outcomes of science teaching. Here is a case where a statement of objectives of science teaching made possible a test of an important hypothesis, with results that are changing the methods of teaching science.

Compare this procedure with the one of which most of us have been guilty. At some time or other we have written a speech on the educational value of chemistry, or of science in general, making the most exorbitant claims. We have said that it makes students think straight in all walks of life. It trains their minds. It gives them a scientific attitude which they will apply to political problems. This elevates our morale. It makes us feel more important. But it doesn't improve our teaching.

Chemists are improving their teaching by patient study of the problems of teaching. The key to improvement is very often the skilful devising of ways of observing and measuring achievements of the desired outcomes. For this reason the devising of tests and other instruments of evaluation is of great importance. A report by Ashford and Shanner[3] is a good example of this kind of work. The examination project recently described by Hendricks and Smith[4] promises to be extremely useful. Over half of the chemists replying to the A. A. A. S. questionnaire marked as "very important" the preparation of tests designed to measure the achievement of students with respect to understanding and use of the scientific method and the ability to do clear thinking.

Within the past few years the number of college teachers who are interested in the scientific study of their teaching problems has grown to the point where they are beginning to come together from various places for a coöperative attack on their common problems. Twenty-two colleges, mainly in the Middle West, have associated themselves under the auspices of the American Council on Education in the Coöperative Study of General Education. These twenty-two colleges each contribute $1000 a year toward the cost of a central service bureau located at the University of Chicago. The staff of the service bureau includes a scientist who works with the science teachers on problems of selecting content for science courses, organizing the material for teaching purposes, and evaluating the results of teaching.

During each of the last three summers about 150 college teachers from the twenty-two colleges and some thirty other institutions have come to the University of Chicago for a five weeks' institute called a Workshop. In the Workshop there has been a group of five to ten chemists, working together on their particular problems.

The University of Minnesota has conducted a Workshop for college teachers during the summers of 1940 and 1941. This past summer there have been Workshops for Junior College Teachers at the University of California and at George Peabody College. The Workshop idea was first tried as a means of aiding high-school teachers to work on their educational problems. As a conservative estimate, there were 130 Workshops for school teachers last summer. In the summer of 1940 a Workshop for High-School Chemistry Teachers was held at Western Reserve University, sponsored by the Division of Chemical Education of the American Chemical Society.

The value of the Workshop lies in the fact that it brings together people with all the special abilities and interests necessary for a successful attack upon educational problems. It attracts college teachers who are interested in the problems of teaching and who have well-defined problems to work on. It provides these teachers with the help of an expert in evaluation procedures—one who knows how to measure and evaluate

[3] ASHFORD AND SHANNER, "Are we teaching our students to distinguish between fact and theory?" J. CHEM. EDUC., **17**, 306–9 (July, 1940).

[4] HENDRICKS AND SMITH, "Better new examinations from old," *ibid.*, **17**, 583–6 (Dec., 1940).

the results of teaching. It also provides these teachers with the help of one who knows about students—one who has studied adolescent development, knows what the basic interests of college students are, what kinds of things they can learn readily, what the various reasons of various kinds of students are for liking or disliking chemistry. Finally, the Workshop stimulates the chemistry teacher by bringing him into contact with teachers of other subjects, all of whom are interested in certain common problems of general education at the college level.

Still another method of improving the college teaching of chemistry is to be seen in the developing interest of several universities in the general problem of the improvement of the preparation of college teachers. Stanford University has a committee on the preparation of college teachers which is studying local problems and trying to plan a program which will make graduate students better prepared for college teaching. The University of Chicago, through its Committee on the Preparation of Teachers, is working on the same problem. This Committee has recently sent an inquiry to all holders of Doctor's degrees from Chicago to find out what experiences have seemed most valuable as aids in teaching. An inquiry is also being made of college presidents and deans to find out what characteristics and what special preparation seem to these people to be possessed by superior college teachers. It appears that a number of graduate schools are beginning to pay serious attention to the problem of preparing graduate students specifically for college teaching.

Thus we observe a number of agencies working on various aspects of the problem of chemistry teaching at the college level. The American Chemical Society is improving the undergraduate teaching of chemistry through its Division of Chemical Education, as well as through its inspection of college departments of chemistry. The colleges themselves are improving their teaching through sending faculty members to summer workshops and otherwise stimulating teachers to try new methods and materials, with a careful study of the results of their experimental work. The graduate schools are paying more attention to the preparation of graduate students for college teaching.

A DEMONSTRATION OF CIS-TRANS ISOMERIZATION

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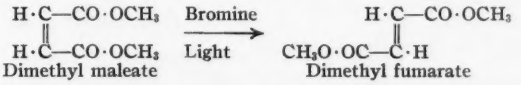
THE catalyzed isomerization[1,2,3] of maleate esters by halogens, hydrogen halides, oxides of nitrogen, sulfur, and various metals suggested the possibility of demonstrating this interesting reaction to a class or laboratory in organic chemistry. Dimethyl maleate is a convenient ester for this purpose because its geometrical isomer, dimethyl fumarate, is a solid which is virtually insoluble in the liquid dimethyl maleate. Trial experiments with various catalysts showed that bromine is one of the most active, especially if the reaction is carried out in a strong light, as indicated by:



Procedure.—Into three 20- by 150-mm. test tubes measure 10-ml. portions of dimethyl maleate. Into two of the test tubes place two drops of a five per cent solution of bromine in carbon tetrachloride. Wrap one of these tubes with dark opaque paper. Place the three tubes in a beaker of boiling water so that each receives about the same light from a 75–100-watt bulb which is placed a foot away. At the end of five minutes remove the tubes and cool with shaking under the cold-water tap. The irradiated sample containing the catalyst rapidly solidifies as colorless crystals of dimethyl fumarate. The wrapped tube containing bromine appears unchanged. The third tube which contained no catalyst but which was irradiated also appears unchanged.

[1] FREUDENBERG, "Stereochemie," F. Deuticke, Leipzig and Vienna, **1933**; Article by KUHN, p. 917.
[2] GRIGNARD AND BAUD, "Traité de chemie organique I," Masson et Cie., Paris, **1935**, p. 1088.
[3] GILBERT, TURKEVITCH, AND WALLIS, *J. Org. Chem.*, **3**, 361 (1939).

These experiments not only show the reaction of cis-trans isomerization but they also illustrate the remarkable effect of a catalyst and of light. Attention should also be called to the fact that the bromine color does not disappear at room temperature. This is in keeping with the general concept that "negatively-substituted" ethylenic bonds are relatively inert in addition reactions. In the sample which undergoes isomerization the bromine color gradually disappears in the course of heating. According to the theory[3] for this process there is first addition of bromine to the ethylenic bond with subsequent elimination. The dibromo intermediate no longer contains a double bond and is therefore incapable of geometric isomerism. When the double bond is re-established, the form produced is the more stable one—in this case the trans or fumarate compound.

If it is desired to prepare the dimethyl maleate and to recover the dimethyl fumarate, the following directions may be used:

58 g. (0.5 mol) of maleic anhydride, 160 g. (200 ml., 5.0 mols) of methyl alcohol, and 4 to 5 ml. of concentrated sulfuric acid are refluxed on the steam bath for 4 to 5 hours. The condenser is then set for distillation and the excess water and alcohol are distilled off. The residue is washed with two 20-ml. portions of water, two 20-ml. portions of five per cent sodium bicarbonate solution, and then once more with water. It is dried over Drierite or anhydrous magnesium sulfate and distilled, the fraction boiling at 200° to 207°C. being collected. Yield, 50 g., 70 per cent of the theoretical.

The dimethyl fumarate prepared above may be easily purified by crystallization from alcohol, m. p. 101°–2°C.

The Many-Acid Problem

KAROL J. MYSELS[1] *Harvard University, Cambridge, Massachusetts*

THERE is a relation between the degree of neutralization and the pH of a solution containing known concentrations of several acids of known dissociation constants. The problem is to find this relation and a method of calculating the degree of neutralization when the pH is given, or inversely the pH when the degree of neutralization is given.

Michaelis[2] points out the importance of this problem and gives a formula for the pH of a solution containing two acids, namely

$$H^+ = \frac{K_1(A_1 - L) + K_2(A_2 - L)}{2L} + \sqrt{\left[\frac{K_1(A_1 - L) + K_2(A_2 - L)}{2L}\right]^2 + \frac{K_1K_2(A_1 + A_2 - L)}{L}}$$

where A_1 and A_2 are the two acid concentrations, K_1 and K_2 the corresponding dissociation constants, and L the amount of base added.

When the general problem is approached in a similar way the resulting equations cannot be solved for H because their degree, with respect to this unknown, is equal to the number of acids present. It is nevertheless possible, as will be shown, to calculate easily the degree of neutralization of any such mixture, when the pH is given. Once this is done for several pH values conveniently chosen, then the pH value corresponding to a given degree of neutralization can be obtained with any desired precision.

Let us consider a solution containing a total concentration A (equivalents) of acid composed of concentrations A_i of the different acids. That is

$$A = \sum_i A_i$$

Let the concentration of alkali be called B. We can write as a first approximation

$$B = \sum_i a_i$$

where a_i represents the concentration of the ionized part of the acid whose total concentration is A_i. Let us introduce the degree of neutralization b for the whole mixture and b_i for each individual acid. Then we have by definition

$$b = B/A \text{ and } b_i = \frac{a_i}{A_i}$$

If we calculate the weighted average of the degrees of neutralization of all the different acids present, we see that it is equal to the degree of neutralization of the whole mixture:

$$\sum_i b_i \cdot \frac{A_i}{A} = b \qquad (1)$$

This result can be obtained by the following obvious substitutions

$$\sum_i \frac{b_iA_i}{A} = \sum_i \frac{a_i}{A} = \frac{\sum_i a_i}{A} = \frac{B}{A} = b$$

In other words the problem of calculating the degree of neutralization of a mixture of acids is reduced to the problem of calculating the degree of neutralization of each acid. This is a simple problem when the pH of the solution is given.

This theorem is general and independent of the nature of the acids present.

We can simplify the problem still further when all the acids involved are monobasic. We have then (if the acids undergo only ionization):

$$K_i = \frac{Ha_i}{A_i - a_i} = \frac{H \cdot a_i/A_i}{1 - a_i/A_i} = \frac{H \cdot b_i}{1 - b_i}$$

or solving for b_i

$$b_i = \frac{1}{1 + H/K_i} = \frac{1}{1 + 10^{pK_i - pH}} \qquad (2)$$

combining (1) with (2) we obtain

$$b = \sum_i \frac{A_i}{A} \cdot \left(\frac{1}{1 + 10^{pK_i - pH}}\right) = \sum_i \frac{A_i}{A} \cdot \left(\frac{1}{1 + \frac{H}{K_i}}\right)$$

which is the desired relation.

In this formula we have A, A_i, K_i which are determined by the conditions of each experiment. The fraction in the parenthesis can be calculated in advance, as a function of pK − pH or H/K. This has been done for pK − pH, which is in general more useful, in the following table.

DEGREES OF NEUTRALIZATION OF A MONOBASIC ACID FOR DIFFERENT PH VALUES

(Values of $\frac{1}{1 + \frac{H}{K}} = \frac{1}{1 + 10^{pK - pH}} = b$ for varying pK − pH)

pK − pH	b	pK − pH	b	pK − pH	b
0.00	0.500	0.80	0.137	1.55	0.027
0.05	0.471	0.85	0.124	1.60	0.025
0.10	0.442	0.90	0.112	1.65	0.022
0.15	0.415	0.95	0.101	1.70	0.020
0.20	0.387			1.75	0.017
0.25	0.360	1.00	0.091	1.80	0.016
0.30	0.334	1.05	0.082	1.85	0.014
0.35	0.309	1.10	0.074	1.90	0.012
0.40	0.285	1.15	0.066	1.95	0.011
0.45	0.262	1.20	0.059		
0.50	0.240	1.25	0.053	2.00	0.010
0.55	0.220	1.30	0.047	2.25	0.006
0.60	0.201	1.35	0.043	2.50	0.003
0.65	0.183	1.40	0.038	2.75	0.002
0.70	0.166	1.45	0.034	3.00	0.001
0.75	0.151	1.50	0.031		

Note: To obtain b values when pK − pH is negative, subtract from 1 the b value corresponding to the absolute value of pK − pH, which is pH − pK.

[1] Present address: 621 Stockton Street, San Francisco, California.

[2] MICHAELIS, "Hydrogen ion concentration," translated by PERLZWEIG, Williams and Wilkins Co., Baltimore, Md., 1926, p. 46.

Thus, with the help of this table, the calculation of the degree of neutralization of a mixture of any number of monobasic acids necessitates only one division and one multiplication per acid present when the pH is known. If the degree of neutralization is known, the pH value can then be easily calculated by any approximation or graphic method.

The table gives also directly the degree of neutralization of a single monobasic acid for any pH.

SUMMER CONFERENCE OF THE NEACT

THE "summer conference" practice is increasing in popularity, and deservedly. The leisurely and pleasurable feeling that accompanies the summer season seems to promote rather than discourage the free flow of thought and discussion. The New England Association of Chemistry Teachers is, as far as we know, the only organization which holds such a conference entirely devoted to the discussion of the problems of chemistry teaching, at both the high-school and college level.

The Association held its third Summer Conference, August 12 to 15, on the campus of the University of Connecticut. It was fully as successful and profitable to all concerned as were the two preceding, at the Universities of Vermont and Maine, respectively.

An excellent program of eighteen formal papers was provided, among which were represented seven industrial concerns and nine universities and research laboratories. A symposium on electrolytes was a central feature, with papers by Andrew J. Scarlett of Dartmouth College, Sidney J. French of Colgate University, John A. Timm of Simmons College, and Laurence S. Foster of Brown University. Evening lectures were preceded by motion pictures. On one of these occasions Games Slayter, of the Owens-Corning Fiberglas Corporation, discussed the recent development of fiberglas with an extensive exhibition of the products. On another evening Kenneth C. D. Hickman, of Distillation Products, spoke on "Science as an Instrument for Peace." Following some examples of "chemical magic" by James W. Yates, of the University of Connecticut, there was a most spectacular demonstration of new methods of extinguishing incendiary bombs, given by Leopold Scheflan, of the Pyrene Manufacturing Company. Anyone who witnessed the result of pouring water on several pounds of burning magnesium will avoid trying it himself!

Round-table discussions, both formal and informal, industrial trips, and a picnic lunch at nearby Knowlton Pond provided lighter diversions.

It is noteworthy that the Conference was attended not only by two hundred high-school and college teachers but also by several industrial and research chemists who apparently came to be "educated." That they were not disappointed would seem likely from the remark of one of these who was overheard to say: "Teachers evidently can teach."

Photo by R. F. Lyons

SOME OF THE OFFICIALS OF THE NEW ENGLAND ASSOCIATION OF CHEMISTRY TEACHERS, AT THE SUMMER CONFERENCE, UNIVERSITY OF CONNECTICUT

Front row, left to right: L. H. Amundsen, University of Connecticut; G. B. Savage, Loomis School (Chairman of Conference); D. W. Putnam, Worcester High School of Commerce; L. S. Foster, Brown University (President); E. H. Coburn, Bulkeley High School

Back row: T. C. Sargent, Swampscott High School (Vice President); Rev. R. G. LaFontaine, St. Thomas' Seminary; J. R. Suydam, St. Mark's School; Elizabeth S. Hollister, Williams Memorial Institute

All who attended are looking forward to next summer's conference, which the Association plans to hold at the University of New Hampshire.

—N. W. R.

"The reason we teach science and take science to the people, as I see it, is because we are convinced that it is the successful method of doing and thinking. Much of our battle upward is a conflict between science and superstition. It is astronomy vs. astrology, fact vs. hearsay, experiment vs. dogma, planning vs. trusting to luck.

"In these perilous times for so many areas of the world, we cannot reaffirm too often that the scientific way is the democratic way. The methods of science will make democracy work if they find their way to the public. Test of reason and experience can weed out the charlatan, the incompetent, and the unworthy in high and low places in our people's business, if we see to it that democracy is free to operate. Freedom to practice the scientific method in the everyday world as well as in the laboratory is of importance equal to freedom of the press and assembly."

—Watson Davis

Cell Formation and Division

J. TRAUBE

Edinburgh, Scotland

THE processes of cell formation and division, so important as biological phenomena, have been frequently simulated, if not reproduced, in a number of non-biological systems. The formation and division of "cells" in such cases is obviously brought about by surface and interfacial forces. These same forces are doubtless effective in all actions occurring in the protoplasm. One stage in the mechanism of cell formation and division is the establishment of "poles" in the protoplasm, which act as central points from which diffusion takes place. These poles may even be formed by gas bubbles.

Among those who have experimented on non-biological systems may be mentioned Leduc, Rhumbler, Bluntschli, Spek, and others.[1] The work of Leduc is perhaps worth special attention. He observed remarkable cell-like formations when water containing China ink was dropped into aqueous solutions of sodium chloride or potassium nitrate. Diffusion effects result in the formation of a number of adjacent "cells" simultaneously, while in the biological phenomenon

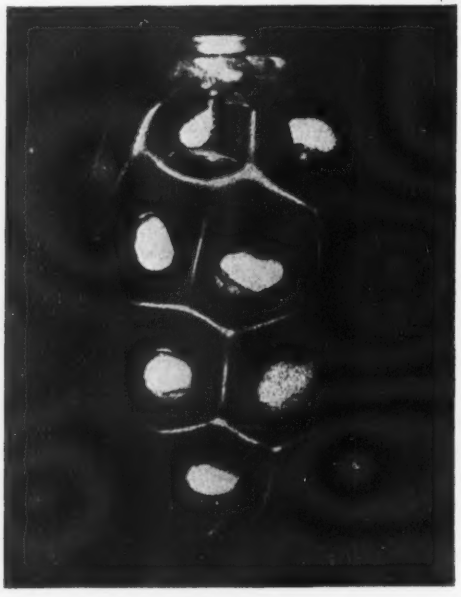


FIGURE 1

cell formation, as a result of division, is of course a consecutive process. Leduc observed a radiation by diffusion and a formation of spindles and astrospheres corresponding to the formation of spindles in biological cells. This radiation proceeded from central poles which can, for example, result from air bubbles. Fields of force, similar to those assumed by Faraday, were produced. Every point at which the concentration is greater than that of the surrounding medium can be considered as a center of attracting or repelling

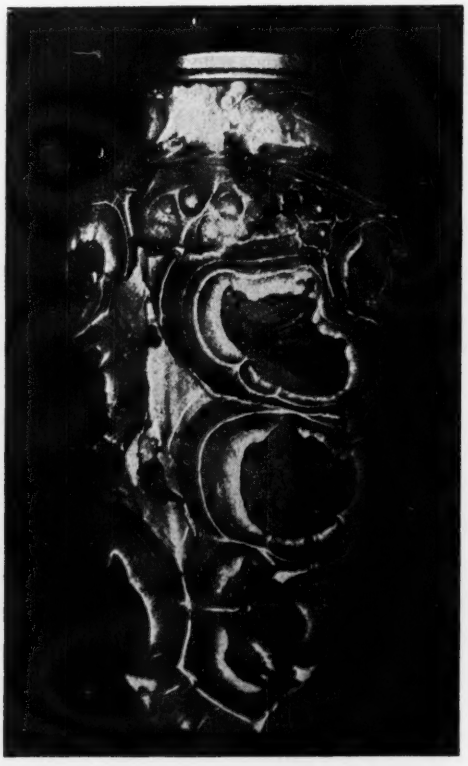


FIGURE 2

force, giving rise to diffusion currents in one direction or the other.

Some years ago the author was trying to develop the technic of producing certain bright-colored formations on glassware.[2] Plaster of Paris was moistened with varying amounts of different salt solutions, applied in spots to the inside of the glassware, and dried. Figure 1 shows a vase made in this way, with a number of nuclei of the plaster on the inner surface, moistened

[1] ABDERHALDEN, Editor, "Handbuch der biologischen Arbeitsmethoden," Urban and Schwarzenberg, Berlin, 1921–23, Abt. 5, Teil 3A.

[2] TRAUBE, "Kolloide Vorgänge beim Binden des Gipses. Strukturen in Gips," *Kolloid-Z.*, **25**, 62–6 (1919).

with ferric chloride solution. After the plaster had partially set, a paste made up with more plaster of Paris moistened with potassium ferrocyanide solution was poured over the inside of the vase and allowed to set over the previous plaster masses. The blue color of ferric ferrocyanide which resulted was separated by white cell walls of a precipitated white substance containing gypsum (the more highly hydrated calcium sulfate). The appearance is very much like that of the cell structures in protoplasm resulting from the colloids there. The plaster nuclei correspond to the nuclei in the protoplasm and in each case there is only one nucleus in each cell. There seems to be a close analogy between these two kinds of cell formation, and especially as regards the forces of diffusion which operate. From the plaster nuclei there is a diffusion of salt to the covering layer of plaster containing ferrocyanide, as well as a diffusion in the opposite direction. As in the case of cataphoretic migration there is a neutral point at which precipitation and deposition take place. It is here that cell walls are formed as a result of diffusion effects. These experiments seem to supplement those of Leduc.

The formations in the second vase (Figures 2 and 3) are especially characteristic. This was made in the same way as the first, just described. One will immediately observe the small cells in the upper part, which are formed from gas bubbles. Each nucleus corresponds to one cell of which it is the parent. Especially noticeable is the beginning of the process of cell division which can be seen in its various stages in adjacent cells. The Liesegang structure is observable in the larger cells, forming a number of parallel cell walls. This effect can only be the result of "rays" from the central body. In biological cell formation this effect consists in the formation of spindles, a process which has its counterpart here in the bluish white radiation surrounding the plaster masses, and in which the individual rays can be easily distinguished by different shades of color.

It is remarkable that the division of cells begins near the nuclei. A thick wall forms between adjacent nuclei, which eventually unites with the cell walls. In this connection, notice particularly the small cells at the top of the vase, as well as the constriction in the cells in which the division appears to be going on.

FIGURE 3

These results seem to the author more striking than those of Leduc in simulating the *consecutive* formation of cells.

INDUSTRIAL SPECIALISTS MAY STILL APPLY FOR GOVERNMENT JOBS

THE Government continues its search for specialists in all branches of industry and business. The Federal Civil Service examination for Industrial Specialists, announced on July 7, 1941, has been amended to remain open for receipt of applications until further notice.

The National Defense Program needs men with experience in one or more of the following fields: iron and steel; non-ferrous metals; machine tools; ordnance; aircraft, marine, and automotive equipment; railroad repair shops; radio and other electrical equipment, supplies, and apparatus; textiles; forest products; paper; printing and publishing; chemicals and allied products; plastics; petroleum and coal products; rubber products; stone, clay, and glass products; leather and its manufactures; food and kindred products.

Salaries range from $2600 to $5600 in the various grades. No written examination is given. Application forms may be obtained from Civil Service Representatives at any first- or second-class post office or at a Civil Service District Office.

CORRECTION

A CORRECTION for "Another Mnemonic," in the July issue, page 346: Oleic acid contains eighteen, not sixteen, carbon atoms, and would therefore not fit into the alphabetical sequence as suggested.

Antiseptics before Lister[1]

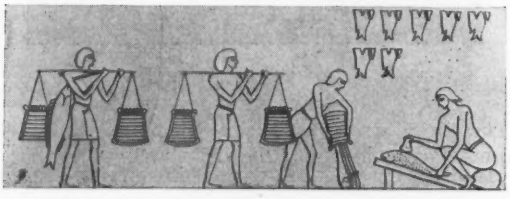
GEORGE GROSS with ED. F. DEGERING

Purdue University, Lafayette, Indiana

THE earliest users of bacteriostatic[2] principles on record are the bees. When an intruder blunders into the hive, he is immediately stung to death and ejected. Dogs, cats, and most other animals lick their wounds to cleanse them and protect them from infection. Woodcocks have been known to cover their wounds with down and several other animals have been known to burrow into mud or damp dirt to cover up wounds.

The earliest use of bacteriostatic principles by ancient man seems to be in the drying of meats. Meat or fish, if left hanging in a dry place away from preying animals and in the presence of sunlight, or if dried over a slow, smoky fire, would resist decay much longer.

The best preserved evidence of ancient bacteriostats is in the Egyptian tombs with their mummies, dried hay, fruits, and smoke-dried fish and meats. The ancient Egyptians believed that the preservation of the body was essential for a happy existence after death. The use of aromatic substances for embalming could perhaps have originated because the Egyptians tried to mask the odors of decaying bodies and noticed that bodies so treated did not decay as rapidly as the others. It seems strange that the Egyptians did not notice the close parallel between decomposition and disease,



ANCIENT EGYPTIANS PRESERVING FISH BY SALTING AND DRYING

and that they did not apply their knowledge of bacteriostats to combat infection in the living.

It is interesting to note that the Guanches, aboriginal inhabitants of the Canaries, practiced methods of embalming similar to those of the Egyptians. Early Ethiopians used a transparent resin while the Persians used a wax in an effort to prevent decay. The most important factor, however, was the exceptionally dry climate.

Smith says that savages from the earliest times used naturally occurring tars and petroleum for wounds and sores on themselves and on their cattle. In an effort to avoid diseases man shunned places where diseases were found and avoided persons who were infected.

About 1200 B.C., when the Children of Israel were moving from place to place in an effort to find the land of Canaan, Moses, the great law-giver and *sanitary engineer*, gave complete directions for the handling of people who had plague, leprosy, running sores, and the like. His methods were those of segregation, confinement, and thorough washing besides appropriate offerings to God. The priests were the judges (or diagnosticians) of the types of diseases, all of which were described in detail.

According to Smith, sulfur was called sacred or divine by the Greeks and was used in purifications. Ulysses, then, burned sulfur in his palace, not to remove the odor of the dead but as a religious ceremony. Cowper translates the passage from Homer's "Odyssey" (Book xxii) thus:

> "Bright blast-averting sulphur. Nurse, bring fire
> That I may fumigate my walls; then bid
> Penelope with her attendants down,
> And summon all the women of her train."

In the beginning of Book xxiii, Pope translates Euryclea's words:

> "Glorious in gore:—now with sulphureous fires
> The dome he purges, now the flame aspires."

The fall of Troy is placed around 1195 B.C., which is somewhere near the time of the first recorded use of sulfur dioxide.

Ultra-violet light, though not known as such, was used for water purification in 800 B.C. In the Sanskrit writing "Surśuta (-samhitā)" one reads, "It is good to keep water in copper vessels and expose it to sunlight and to filter through charcoal."

The Hindu surgeon, Susrusta, sometime before 500 B.C. recommended that the operating room be fumigated before and after each operation. The Atharva Veda, sometime before 500 B.C., states that foul water may be cleansed by isolation and by dipping hot copper in it.

A century or so later the "Father of Medicine," Hippocrates, advocated the burning of sulfur and tar to drive away various pestilences.

Dunker gives this description of the methods of Hippocrates:

[1] An abstract of a portion of a thesis submitted to the faculty of Purdue University by George C. Gross in partial fulfilment of the requirements for the degree of Master of Science, June, 1938. Presented before the Division of the History of Chemistry at the ninety-eighth meeting of the A. C. S., Boston, Massachusetts, September 12, 1939.

[2] Bacteriocide and bacteriocidal will be used to designate the agent or action which destroys or kills bacteria. Bacteriostat and bacteriostatic will be used to designate the agent or action which inhibits the growth of bacteria. In modern terminology antiseptic and preservative are synonymous with bacteriostatic action, and germicidal and disinfection are synonymous with bacteriocidal action. In this paper, however, the terms are the same as those used by the sources from which they were obtained.

"Let us consider the pseudo antisepsis of the ancients as proposed by Hippocrates. Knowing nothing of the cause of infection, Hippocrates applied to wounds substances which are now recognized as antiseptics. However, the instruments and dressings employed were themselves never sterilized or protected from contamination. These attempts can hardly be considered truly antiseptic. On the other hand, an examination of ancient writings assembled by Galen (born 130 B.C.) leads Anagnostakis (1889) to insist that Hippocrates was the originator of the idea of antiseptic treatment. This author asserts that in the surgery of Hippocrates, the drying of the wounds constitutes the antisepsis and the drying agents are accordingly the antiseptics. . . . The complete wound treatment of Hippocrates was as follows:

1. After stopping the hemorrhage, wash the area with warm wine, in eye injuries use a weak salt solution.
2. Wipe dry with a linen cloth.
3. Anoint the wound surfaces with tar or with a solution of a copper salt mixed with aromatics and bitters.
4. Reunite the borders of the wound (suture).
5. Dust with antiseptic powders such as copper salts, aromatics, and resins.
6. Cover the area with a tar plaster.
7. Coat the surrounding parts with a cerate to prevent the entrance of air.
8. Apply compresses soaked in wine.
9. Cover the entire area with a linen bandage."

Hippocrates advocated the use of astringents, wine, alum dissolved in vinegar, galls, and the green bark of a fig tree (tannins). Another dressing was prepared by placing sour grapes in a vase of red copper in the sun and adding honey, myrrh, niter, and a small quantity of turpentine. As first-aid measures on the battle field, Greek history tells of the use of wine and the juices of "healing herbs."

Another custom, undoubtedly borrowed from the bees, used in Greek and Roman times, was the preservation of the dead in honey. Virgil refers to this in the following lines:

> "Grant the corse torn by ravening fangs a curse,
> Is hence no ill in funeral flames to burn,
> Or, pent in cold obstruction, stiffening lie
> Immers'd in honey, while entombed in stone."

Josephus, the great Jewish historian, tells of the preservation of the Jewish king, Aristobulus, in honey until his burial.

The story of the Good Samaritan as told by Our Lord indicates the first-aid treatment and methods, using wine and oils, generally employed by the peoples of this time.

Ovid, who lived about the same period, tells of shepherds who used burning sulfur to purify their wool from disease. In "*Fasti*" he says, "Let blue smoke arise from the burning sulphur, and let the sheep bleat when touched by the smoking sulphur." Undoubtedly it was used for a similar purpose long before Ovid's time.

The next person to make a contribution to "antiseptics" was Celsus, who lived in the first century A.D. He described drugs and included, under styptics, the drugs which affected pus formation. His treatment of wounds was based on two principles, care for hemorrhage and reduction of inflammation.

Turpentine from *Pistacia terebinthus* and myrrh were added to wines in Roman times to prevent them from souring. Pitch and crude pine tar, too, were used to control fermentation. The Romans and Greeks also had laws regarding the size and spacing of the houses; their elaborate sewerage and pure water systems are well known.

EARLY GOTHS CATCHING FISH AND PRESERVING THEM BY SMOKING

Galen (A.D. 130–200), the great pharmacist, recommended oils and wines for the treatment of wounds. Around A.D. 300 Dioscorides is supposed to have used sea salt as an antiseptic on fresh wounds as a powder or as a solution. After an operation he sprinkled a little powdered salt in the wound.

Oribasius in the third and fourth centuries recommended various copper salts for preserving moist surfaces. Copper acetate was regarded as a drying agent and as a slow detergent.

In the seventh century Paul d'Egine recommended the treatment of abscesses with heat.

The Anglo-Saxons used mainly astringent substances. The following recipes are taken from a seventh century leach book:

"1. A wound salve: Take seed of waybread, bray it small, shed it on the wound; so it will be better.

"2. For cleansing of a wound: Take clean honey, warm it at the fire, put it then into a clean vessel, add salt, and shake it till it have the thickness of brewit, smear the wound therewith, when it turneth foul. If there be a bone breach in the head, pound mayth and goutweed well in honey, then add butter; that is a good salve.

"3. Again, a wound salve: The groundsel which waxeth in highways, that is good for a wound salve and ribwort and yarrow and githripe; pound all the worts, boil in butter and squeeze through a cloth."

Mugwort, alecost, and alehoof derived their Saxon names from their use in preserving beers and ales.

During the middle ages, when monasteries were the hospitals and monks the doctors, the balsamic dressing known as Friars Balsam was compounded.

Rhazes, the Arab (A.D. 850–932), first obtained alcohol by distillation and employed it alone or mixed with astringent plants. Another Arabian physician, Albaceus (A.D. 936–1013), used a pad of cotton wool soaked in rue oil alone or mixed with an astringent wine. He was

the first to recognize that it is dangerous to leave an open wound exposed to the air.

In the thirteenth century William of Salecto used a mixture of rose oil and white of egg, applied with a feather. Nicolaus, a German barber surgeon, introduced warm hempseed oil in the treatment of gunshot wounds. Guy de Chauliac, a fourteenth century surgeon, washed a wound with hot red wine. Around the wound but not on it he applied "a mixture of oil of myrtle and oil of roses mixed or a mixture of oil and vinegar."

DOG LICKING A WOUND TO WHICH AN ANGEL APPLIES A DRESSING
From a woodcut of the fifteenth century

For wound treatments Braunshing recommended that warm oil of violets be poured into the wound, that camphor or turpentine be used as a local dressing, and that *the wound be left open*. In 1365 John of Burgundy suggested that the air in the room of a plague patient be purified by burning juniper branches, and that powders be thrown on hot coals to provide fumes for the patient to breathe.

Remedies for plague were sponges dipped in rose water or in vinegar in which wormwood and rue had been boiled. The sponge was "to be smelled often."

Little progress was made in the fifteenth century. The trend was retrogressive. The general treatment was cautery to stop hemorrhage and a dressing of which the following is representative: dried earthworms in a powder, Armenian bole, camphor, and oil of roses.

Paracelsus in the first part of the sixteenth century used lead acetate on wounds. Blondus later suggested the use of water alone.

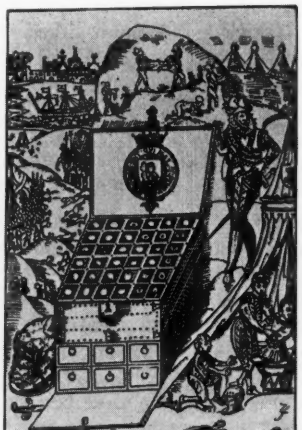
One of the greatest advances was made by the great French surgeon, Paré (1510?–90). He believed, as did most other surgeons of his time, that gunshot wounds were poisoned. Accordingly the treatment consisted of boiling oil and pitch. This is his story of how the truth about gunshot wounds was shown:

"It chanced on a time that by reason of the multitude that were hurt I wanted this oil (Oyl of Elders Scalding hot with a little Treacle mixed therewith). Now because there were some few left to be dressed I was forced . . . that I might not leave them undrest, to apply a digestive made of the yolk of an egg, Oil of Roses, and Turpentine. I could not sleep all that night for I was troubled in mind, and the dressing of the precedent day (which I judged unfit), troubled my thoughts; and I feared that the next day I should find them dead, or at the point of death by the poison of the wounds. . . . Therefore I rose early in the morning. I visited my patients and beyond expectation I found such as I had dressed with the digestive only, free from vehemency of pain, to have had a good rest and that their wounds were not inflamed . . . but . . . the others that were burnt with the Scalding Oyl were feverish, tormented with much pain and swoln. When I had many times tried this in divers others, I thought this much, that neither I nor any other should ever cauterise any wounded with gunshot."

In 1552 he finally gave up cauterization of any kind of wound and sewed the opening up. Later Paré stated that all he could do was to apply a digestive and await the signs of "laudable pus."

Jones records that in 1549 after the plague in Malta the buildings were washed with soap and lye, then with lime. The drains were cleansed and flushed. The buildings were fumigated with a mixture consisting mainly of sulfur, aromatics (pepper, ginger, etc.), inorganic sulfides, bran, and sawdust. When this was burned, it gave off antiseptic fumes.

A Swiss surgeon, Felix Wuertz, in 1563 advocated *crocus martis* (oxide of iron), alum, and hair of white rabbit. He stated that honey was the best salve and deplored the use of the dirty, oily mixtures and salves then in vogue.



MILITARY MEDICINE CHEST—1588
Fabricius, a noted Swiss physician of the 16th century, recommended that the military chest should be furnished with no less than 362 varieties of medicine, some of which contained as many as 64 ingredients. The complexity of arrangement, the huge bulk and great weight, the liability to breakage, and the complicated inconvenience of medicine chests persisted until the introduction of "Tabloid" Medical Equipments

During the sixteenth and seventeenth centuries witchcraft and superstition flourished more than ever before. Mysterious ointments to be put on with certain magic words were popular. Ointments composed of human fat and the fat of various animals, such as goose grease, were looked upon as potent healers.

APPLICATION OF THE ACTUAL CAUTERY TO A WOUND
From a woodcut of the sixteenth century

One of the greatest fakes in vogue was Kenelm Digby's Sympathetic Powder. This was a magic powder of unknown composition which was applied to the weapon instead of the wound. Its greatest asset was that it allowed natural healing to occur, as the wound was merely washed and bandaged.

During this period the explorers reported that the natives of Peru threw cinchona logs in fetid pools to purify them. The action may be attributed to the tannin and quinine.

It was during this century that air was first declared to be infectious. Also, progress was made in the reassertion that nature played the principal part in healing a wound and that a physician had no power to make tissue. The idea that a wound could be fed was dropped.

The seventeenth century saw the beginning of modern "antiseptics." Leeuwenhoek developed the compound microscope. In 1675 he first observed microorganisms. Bacteriocides progressed along the same general lines as before, as shown by the record that Wiseman (1682) used turpentine and various astringent powders and lotions.

During the Black Plague in England in the seventeenth century absurd methods supported by absurd theories were used to combat the disease.

Sir John Colbatch in 1698 recommended the use of sulfurous acid internally to help destroy malignant fever. He also describes a medicant which "gives almost the modern (1895) aseptic condition of the wound."

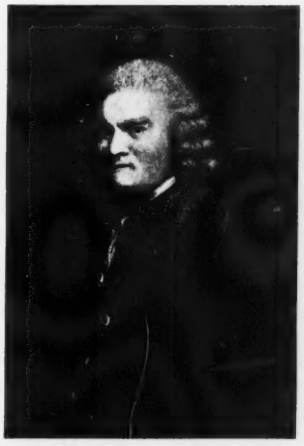
In 1706 Paramus used a lotion of his own which he claimed did not putrefy. Delamotte used brandy and tincture of aloes as a wound dressing. In 1721 Place had a wonderful idea about the logic behind all of these wound disinfectants. He said,

> "As this phenomenon shows the motion of the pestilential poison to be putrefactive, it makes the use of antiseptiks a reasonable way to oppose it, and whatever resists and is preservative against putrefaction, admits not of the generation of insects. If this hypothesis is proceeded upon, our proper and promising materials to yield medicine and for physical preparations against it, such as cedar, Irish oak, cinnamon, spices, and what was used by the ancients in their embalmments of dead bodies, for the same virtues that preserved dead bodies from insects and putrefaction I know no reason why they should not preserve the same bodies living from the same thing."

If his theories had been put into practice, the pseudo-antiseptic surgery of the day might have had better results.

Copoiba was used by Turner in 1729. Balsams still held sway as shown by the records of Col. de Villers (1741). He also recommended dressings of tutty powder, white lead, burnt alum, and burnt lead. He used bandages soaked in lukewarm wine or brandy.

The first attempt to compare the relative bacteriostatic action of various salts and drugs was made in 1750 by Dr. John Pringle. He first disproved the chemist's point of view that alkaline salts promoted putrefaction. Then he used a comparative method to determine the effectiveness of different materials. In his paper, "Memoir sur les substances septiques et antiseptiques," he describes his method and results.



SIR JOHN PRINGLE, FAMOUS ARMY SURGEON (1707–82)

In 1766 Madame d'Arconville published the results of ten years of work in her book, "Essai pour servir à l'histoire de la Putrefaction." She received her ideas from Sir John Pringle's work. Using a modification of his method for all of her experiments (over 300) she came to the following conclusions: While metallic salts are too poisonous to use, their solutions can be

diluted so as to make them useful in preserving specimens; there is no need of using metallic salts when there is a large number of other things that will work just as well; and air must be excluded in order to prevent putrefaction.

In 1766 MacBride again reported that "acids and alkalies destroy putrefaction and give back softness to the affected parts but not in live bodies." He said that vitriol, sea salt, vinegar, and lemon juice would keep meat fresh for four days and that claret and Portuguese white wine were the best of the wines for this purpose. Smith in the same year recommended heated potassium nitrate as a disinfectant for wards and hospitals. The Academy of Sciences at Dijon, in 1770, offered a prize for the best treatise on Antiseptics. A French investigator, Bordenave, won the prize. He concluded that investigation of dead flesh was futile if one attempted to apply the conclusions to putrefaction in living wounds. He sought to prevent putrefaction with astringent substances. Seemingly he also recognized the value of keeping air out of a wound. In 1771 there was an extensive use of salts, sulfur dioxide, and sulfurous acid. Lambert and Percy investigated the infallible remedy of an Alsatian miller and found that it was pure river water poured on with certain incantations. The water worked just as well without the incantations.

Hydrochloric acid gas was recommended by Guyton de Morveau as a means of fumigation. He fumigated both full and empty wards with a brazier containing hot sand and mixtures of nitric acid and salt or sulfuric acid and salt, though he recognized that salt mixtures with nitric acid gave off chlorine and oxides of nitrogen and that these were not as safe a fumigant as the hydrochloric acid gas.

In the latter part of the eighteenth century brandy and water were popular remedies. The surgeon of Napoleon's "Grande Armée" endorsed the use of pure water, with perhaps the addition of alcohol or extract of lead. After the study of the Alsatian miller's remedy and their later experiments, Percy and Larry advocated only pure water in the treatment of gunshot wounds. Alcohol and herbs were discarded, though alum, brandy, salt, and extract of lead were added to water when good water was not available. At the end of the eighteenth century Bassi introduced injections of mercuric chloride to cure ulcers.

The beginning of the nineteenth century showed little progress in the rational use of bacteriocides. By 1801 Chisholm was using sulfur, gunpowder, tobacco smoke, and vinegar.

Appert in 1804 discovered that meat and vegetables, when placed in carefully sealed containers and dipped in boiling water for an hour, would keep indefinitely without fermentation or putrefaction. Gay-Lussac reported on this at the request of the French Government and expressed the opinion that as oxygen was absent in the vessels, oxygen was necessary for putrefaction.

Catbush recognized the relation of unclean water and insanitary dwellings to the spread of disease, and ordered that drinking water be treated with lime and sleeping quarters on ships be whitewashed. Von Rern (1809) endorsed the use of warm water for surgical dressings, followed by heat and rest. This was a general method of treatment up until the time of Lister. In 1815 the antiseptic and preservative properties of coal tar were discovered by Chaumette. Alcock (1827) published his opinions on the use of sodium and calcium compounds of chlorine (hypochlorites?), and emphasized their antiseptic properties. The *Lancet* severely criticized his views. Robertson of the convicts' hospital ship, *Canada*, reported that chloride of lime is eminently useful in preventing the extension of infectious diseases. In 1830 Reichenbach discovered the antiseptic powers of creosote.

The *Lancet* in 1832 discussed the danger of wounds received during autopsy and advised immediate cauterization with silver nitrate. In 1832 the English Board of Health gave serious consideration to the fumigation of all incoming ships with chlorine and decided it to be worthless. Dr. Henry in 1831 tells of the disinfection of clothes by dry heat at 93°C. which proved to be an effective treatment for garments worn by scarlet fever patients.

Oliver Wendell Holmes published an essay, "The Contagiousness of Puerperal Fever," which was one of the most hotly debated papers of his time. Semmelweiss, an assistant in the first obstetrical ward of the Allegmeines Krankenhaus, noticed that the mortality in the ward not visited by medical students was much less than in those visited frequently by the students, who came directly from the post-mortem examination of women who had died of puerperal fever. He considered the cadaveric poisons to be the cause of the disease and, without any scientific evidence to guide him, ordered the students not to touch a woman until after washing their hands well in chlorine water. Later he used chlorinated lime instead. The results were amazing; the death rate dropped from 11.40 per cent to 1.27 per cent in two years. Like most pioneers, Semmelweiss became involved in bitter arguments, and died in an insane asylum in 1865. It was discovered later that an unknown French physician used calcium hypochlorite a few years before Semmelweiss. However, the medical profession should be censured for not having adopted his practices when they were so well proved.

Sir Guye LeFévre in an article in the *Lancet* in 1834 tells of the use, in Germany, of potassium iodide and mercuric chloride in pills for syphilis, and the use of chlorine water in St. Petersburg as a gargle. This was sometimes sweetened, but sugar was known to reduce its activity. John Bell, the famous nineteenth century surgeon, recommended the use of "acrid balsams" and his son, Charles, used spirits. Bishop Berkley extolled the use of tar water.

Demaquey used glycerin, and at about the same time (1835) iodine was introduced. Carbolic acid was discovered experimentally in 1834 by Ringe to have dis-

infecting properties. Bayard applied a disinfecting powder containing tar in 1844. Joseph Jones, a New Orleans surgeon (1855), used tar, carbolic acid, arsenious acid, and mercuric chloride for preserving specimens. At the same time Angus Smith investigated the properties of carbolic acid, which was tried at St. Mary's Hospital in London in 1855. In 1857 Calvert of Manchester used the material for preserving flesh. Smith recommended its use in sewers, and McDougal used coal tar and lime for sewers at Carlisle. In 1859 Messrs. LeMaine and LeBoeuf of Paris applied a soap emulsion of crude carbolic acid to gangrenous ulcers. Ruchenmeister used it for surgical disinfection and to arrest putrefaction. In 1860 Lemaire demonstrated the use of coal-tar applications in treating wounds. Being a representative mixture of the time, Lemaire's coal-tar saponin is included. Keen says that it was a mixture of saponin, alcohol, carbolic acid, benzene, and naphthalene. Another representative mixture of the period just before Lister is that of Werner de Mulhause:

Venice turpentine	1000 parts
Sodium bicarbonate	25 parts
Dissolve in distilled water	10 liters

About this time a few surgeons retrogressed by trying to use absorbent earths. In 1858 Ditz started using the material; Schroeder followed his example in 1863; and as late as 1872 Hewson of the United States used yellow clay.

Pasteur, after his long bacterial studies, decided putrefaction was but fermentation of flesh which could be prevented by destroying the germs. For this reason he, in 1862, advocated the use of boric acid for surgical purposes.

Lemaire in 1863 published a paper on the destructive action of carbolic acid on low forms of life and recommended the application of it to ulcerating and suppurating surfaces. Coal-tar applications were used to a limited extent by a large number of surgeons. Carbolic acid was used for disinfecting stables in cases of disease. Poli of Milan made observations in the period 1857–61 on the use of sulfurous acid and sulfites in arresting fermentation.

During the War between the States (1860–65) the South was shut off from medicinals. For antiseptic dressings the surgeons used cold water, later decoctions of red oak bark, and sometimes dilute solutions of sodium bicarbonate. A buckeye lotion was used for gangrenous ulcers and mutton suet and sweet gum for sores.

Harris of New York recommended during the cholera plague of 1865 the disinfection of excreta with potassium permanganate, carbolate of lime, iron sulfate or protochloride, coal tar, carbolic acid, and Laborraques' solution (sodium hypochlorite). In 1866 the Annual Report of the Metropolitan Board of Health said that calcium and sodium hypochlorites would not give complete and permanent protection against cholera. Some doubt was thrown on the use of carbolic acid by M. Chevreul. A report given in 1867 in Germany on the prevention of the spread of cholera by careful attention to sanitation said all excreta were disinfected with sulfate of iron, carbolic acid, and similar products, and covered with powdered mineral charcoal. The next year M. Bonjean recommended the use of disinfectants in night vessels for the control of cholera. He also stated that carbolic acid was worthless, and the reviewer in the *Lancet* remarked:

"Be this as it may, it is perfectly true that fashion and crying up have an enormous deal to do with the use of disinfectants. We should not immediately a new one is produced forget chloride of zinc, manganate of potash, charcoal, and green vitriol."

McCulloch states that during this period just before Lister disinfectants were commonly used, as shown by various articles in the medical journals of the period. Gascoyne reported that injections of strong solutions of silver nitrate into the urethra seldom prevented gonorrhea. In the same year (1867) Watson recommended potash and carbolic acid solutions and the injection of tincture of iodine.

Hence the time was long overdue for some genius to arise and bring order out of the theory and practice of antiseptics, and that genius was Lord Lister.

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What's Been Going On

(*Continued from page 452.*)

affected by a large number of bacteria, nor is its potency destroyed by the peptones of the blood. It appears to be non-toxic.

As contrasted with the war of 1914, the current conflict has found our pharmaceutical houses in comparatively good condition to handle the demands for antiseptics. While no final choice of an antiseptic has been reached, the current practice seems to be narrowed down to the use of the compounds already considered along with proflavine, brilliant green, hydrogen peroxide, azochloramide, and sterile saline solution.

Doubtless, new and still more effective antiseptics will be added to the list before the war is over.

—ED. F. DEGERING

Properties vs. Performance of Present-Day Anti-freeze Solutions[1]

D. H. GREEN, H. LAMPREY, and E. E. SOMMER

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SINCE approximately two-thirds of the energy in the gasoline used in operating an automobile engine is converted into heat, it is necessary to provide special cooling facilities to prevent the metal parts from reaching excessive temperatures. The method generally used is an indirect one involving the transfer of heat from the engine to a liquid, and the cooling of the liquid by the air through the use of a separate apparatus—the radiator. Water was naturally selected as a cooling medium because of its availability and relatively high heat transfer properties. However, water has certain inherent shortcomings, the most important of which are its high freezing point and its corrosive action on the metal parts of the cooling system, which may result in rust clogging and metal perforation. These two major disadvantages are largely overcome by adding to the water materials to prevent freezing in the winter and special chemical in-

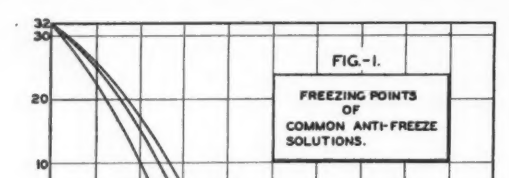


FIGURE 1.—FREEZING POINTS OF COMMON ANTI-FREEZE SOLUTIONS

gredients to inhibit corrosion both in anti-freeze solutions and in water alone. It is with the former of these, the anti-freezing materials, that the present discussion is primarily concerned.

While the first requirement for an acceptable anti-freeze material is that it will adequately lower the freezing point of water, to protect against lowest winter temperatures, it is also highly desirable that it reduce the corrosive tendency of water, and of still greater importance that it not impart any undesirable properties to water that would interfere with its primary function of cooling the engine efficiently. Oils, sugars, and inorganic salt solutions are generally regarded as unsatisfactory anti-freeze materials by the motor car manufacturers, and the objections to their use have been pointed out in the literature of the Society of Automotive Engineers (*1*) and the United States Bureau of Standards (*8*). At present, approximately one-third of the cars requiring anti-freeze are protected with ethylene glycol base products and most of the remaining two-thirds employ methanol or ethanol solutions. The remainder of this paper is confined to a practical evaluation of these latter three materials.

FREEZING POINT

The anti-freeze effectiveness of methanol, ethanol, and ethylene glycol is shown in Figure 1. These curves bring out several interesting facts. First, methanol gives the greatest freezing protection per unit volume, followed by ethylene glycol and then ethanol. Second, all three liquids are capable of depressing the freezing point of water to the lowest atmospheric temperatures likely to be encountered. The first classification is based only on freezing protection per gallon and does not take into consideration the extra quantities of the low boiling-point alcohol anti-freeze solutions required after the initial filling because of boil-away losses, or the superiority of the comparatively high boiling points of ethylene glycol solutions in preventing such losses.

Unlike water, anti-freeze solutions do not solidify when exposed to temperatures slightly below the freezing point but instead tend to form a slush. This raises the question of cooling system operation at these sub-freezing temperatures. To investigate this problem, tests were conducted on late models of popular cars in the specially built "cold room" shown in Figure 2. The minimum temperature to which solutions of the three

TABLE I

MINIMUM SAFE TEMPERATURES OF ANTI-FREEZE SOLUTIONS

Anti-freeze	*Freezing Point*	*Minimum Temperature*
Methanol	0°F.	−2.5° to −5.5°F.
Ethanol	0°F.	−5.5° to −8.0°F.
Ethylene glycol	0°F.	−8.0° to −11.5°F.

[1] Presented before the Division of Chemical Education at the ninety-ninth meeting of the A. C. S., Cincinnati, Ohio, April 9, 1940.

types of anti-freezes having a freezing point of 0°F. may be safely exposed, without giving rise to overheating or other difficulties immediately afterward when the engine is started, is shown in Table 1.

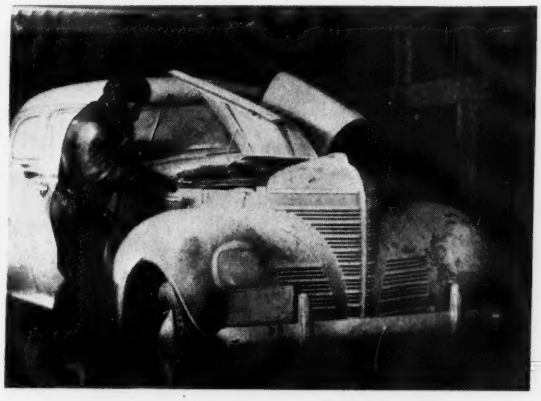


FIGURE 2.—COLD ROOM

The lower the freezing point of the anti-freeze solution used, the farther below this freezing temperature it is possible to expose the solution without fear of overheating, resulting from circulation restricted by ice crystals or slush ice, after the engine is started. This is illustrated in Figure 3 for ethylene glycol, where the true freezing points of solutions (upper curve) are compared with the minimum safe temperatures.

These data establish that such broad generalizations cannot safely be made as are found in the literature (*2*) to the effect that "the point at which enough ice is formed to stop flow lies about ten degrees below the freezing point." Furthermore, it is evident that the only practical basis for providing anti-freeze protection is the true freezing point.

CHEMICAL STABILITY AND NON-CORROSIVENESS

While water itself is chemically very stable, it attacks certain cooling system metals quite vigorously under the influence of heat and aëration—conditions constantly present in an automobile cooling system. Heat is provided by combustion of the fuel, and air is continuously introduced into the cooling system of even a perfectly normal engine by entrainment in the top radiator tank. In a poorly serviced engine, this aëration may be greatly aggravated by leaks which suck air into the cooling system, especially at the water pump seals. Moreover, improperly tightened cylinder heads or leaky cylinder head gaskets may permit the seepage of acidic exhaust gases into the cooling solution, thus augmenting the action of heat and aëration on corrosion. To reduce this corrosion it is necessary to add to the water corrosion inhibitors during the summer time, and to use chemically treated anti-freezes in winter.

The necessity of using proper inhibitors can be demonstrated in laboratory corrosion test equipment. Test data are shown in Table 2, where corrosion is expressed as the loss in weight of metal specimens after two hundred hours of immersion in heated and aërated cooling solutions.

TABLE 2

CORROSION TESTS ON TREATED AND UNTREATED ANTI-FREEZE SOLUTIONS*

Test No.	Weight Losses in mg. per 12 sq. in. per 200 hours at 170°F. Iron	Aluminum	Copper	Brass	Solder
1. Untreated methanol	1995	49	29	43	24
2. Commercial methanol, inhibited	1	1	10	2	10
3. Untreated ethanol	1390	21	42	4	18
4. Commercial ethanol, inhibited	0	3	23	8	23
5. Untreated ethylene glycol	793	45	101	101	267
6. Inhibited ethylene glycol	0	0	1	1	40
7. Distilled water	1524	5	93	93	234
8. Inhibited water	0	4	32	20	32

* All solutions except No. 7 and 8 of freezing point 0°F.

While such tests as these are well adapted for rough estimations, it is necessary to supplement tests in glass apparatus with apparatus more nearly reproducing conditions in automobile cooling systems if more accurate and broader knowledge is desired. A metal "hot spot" unit, a circulating apparatus, a small, low horsepower, single cylinder engine, and a full-sized automobile engine attached to a hydraulic power absorption device (Figure 4), are all used in anti-freeze testing. This latter unit or dynamometer duplicates very closely operation actually experienced in practice, although in the last analysis, statistical data from car fleet tests are necessary.

Two types of inhibitors are in general use—soluble

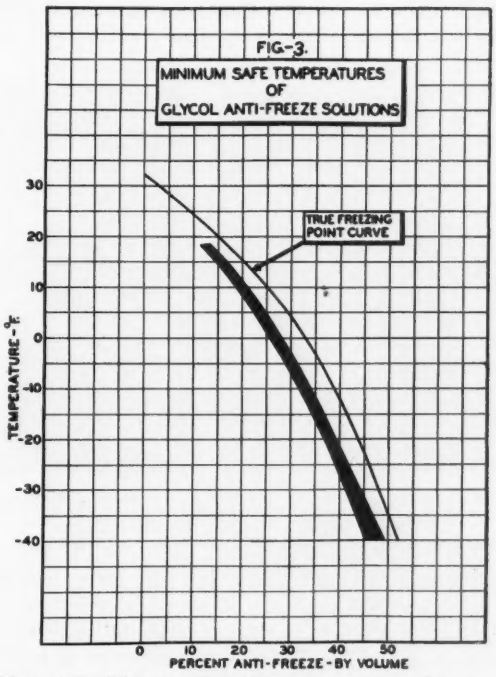


FIGURE 3.—MINIMUM SAFE TEMPERATURES OF GLYCOL ANTI-FREEZE SOLUTIONS

oils and salts—the oil-type corrosion inhibitors being widely used in proprietary anti-freeze preparations. It has been conclusively shown that many oils cannot be recommended, especially if used in excessive concentrations, because of their injurious action on rubber parts of the cooling system. A series of 10,000-hour circulating tests on over 100 different grades and makes of radiator and car heater hoses has shown that hose failures are primarily related to the grade of rubber and type of hose employed rather than to the type of solution used in the cooling system. However, it was found that one popular brand of ethylene glycol anti-freeze, treated with the proper type and amount of oil inhibitor, actually reduced the rate of rubber deterioration over that occurring with water. Thus, 22 per cent of the radiator hoses failed in the water test and only seven per cent in the treated ethylene glycol test. The tests also showed that one methanol base anti-freeze with a salt inhibitor was quite similar in action to water, and one ethanol base anti-freeze inhibited with a large quantity of mineral oil caused a pronounced softening of the rubber. At the end of the test it was found that more than twice as many hoses had failed with this particular ethanol base anti-freeze, as compared with either water or the ethylene glycol anti-freeze. Figure 5 shows a specimen of failed hose from this test.

The other common type of inhibitor is the salt type which, if used, must be selected with care. For example, the use of a chromate inhibitor has been found to do more harm than good when used in improper concentrations (*3*, *4*). Chromates, because of their oxidizing nature, induce inhibitor depletion and may bring about foaming and should, therefore, not be mixed with either ethanol, methanol, or ethylene glycol anti-freezes.

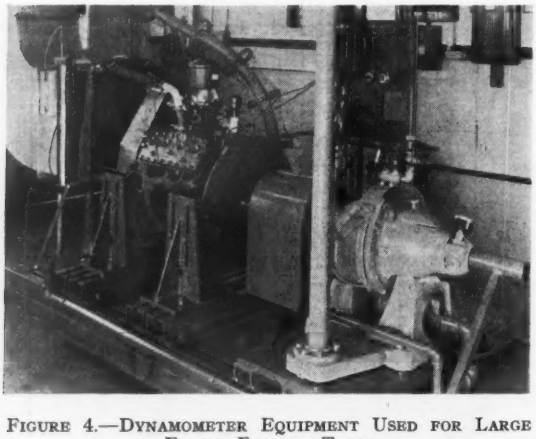
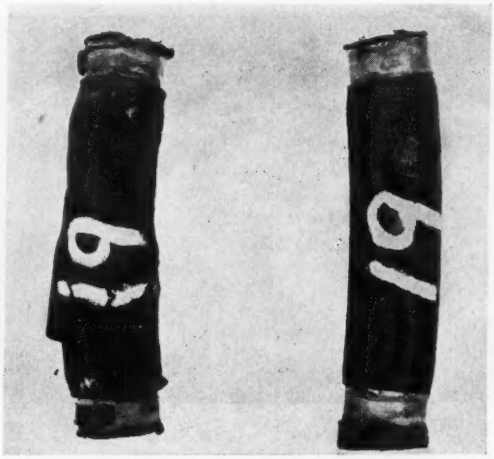


FIGURE 4.—DYNAMOMETER EQUIPMENT USED FOR LARGE ENGINE FOAMING TESTS

Dynamometer, laboratory, and field tests show that all inhibitors are gradually depleted in service. This situation has resulted in the recommendation of leading automotive and anti-freeze authorities that anti-freeze solution which has been used all winter should be discarded in the spring; a special summer inhibitor should be installed with a fresh filling of water for warm weather driving, and fresh unused anti-freeze material should be put in in the fall, to *insure* effective full-strength corrosion protection in the cooling system at all times. Tests have shown that it is generally impracticable, and sometimes even harmful, to attempt rejuvenation of a used anti-freeze solution by addition of corrosion inhibitors.



(*a*) (*b*)

FIGURE 5.—HOSE TEST SAMPLES
(*a*) Water; (*b*) Ethylene glycol

FOAMING AND LEAKAGE

In the preceding section, it was pointed out that air is continuously entrained in the cooling system even under normal conditions as a result of turbulence in the top radiator tank. This air, caught in the form of bubbles, not only increases corrosion but may under certain conditions cause solution loss through the overflow pipe by increasing the cooling solution volume to the point of spillage.

Experiments in leak-tight cooling systems have shown that the air entrained in the cooling liquid during perfectly normal high-speed engine operation may exceed one per cent of the total volume of the cooling system. In Figure 6 are shown photographs of solution passing through a glass tube inserted in the upper radiator hose. The extremely fine dispersion of air caused by top tank turbulence can be seen in the first picture. Reducing the engine speed, and consequently the turbulence, results in the perfectly clear solution shown in the second picture.

Untreated ethylene glycol anti-freeze solutions have markedly greater foaming or "air-entraining" properties than does water and must be properly "defoamed" before they are suitable for use. The excessively large overflow losses from foaming of untreated ethylene glycol solutions due to normal aëration and the effectiveness with which anti-foam agents reduce these

losses are shown by hitherto unpublished dynamometer test data in Table 3.

TABLE 3

COMPARATIVE FOAMING DATA IN 1939 COOLING SYSTEM*

Anti-freeze Type	*Solution Temperature*	*Solution Loss After 1000 Miles*
Untreated ethylene glycol	180°F.	1000 cc.
Improperly treated ethylene glycol	180°F.	4000 cc.
Properly treated ethylene glycol	180°F.	75 cc.

* Dynamometer test; 60 m.p.h., solutions of f.p. 0°F.

Dynamometer foaming test apparatus is shown in Figure 4.

There is much confusion and difference of opinion regarding the comparative leakage rates of ethylene glycol solutions and water from small crevices in the cooling system. To clear up this matter, their leakage rates were measured from leaks of various types and sizes and under a variety of conditions. Some of these tests were made in laboratory apparatus and some in cars. These measurements show that untreated ethylene glycol solutions tend to leak faster than water from a cooling system, but that glycol solutions properly treated with suitable anti-leak agents exhibit leakage rates considerably less than water. One popular brand of treated ethylene glycol can be shown to have a leakage rate of only 30 to 50 per cent that of water.

BOILING POINT

To understand the importance of the boiling point of anti-freeze solution, it is first necessary to know something about the solution temperatures occurring in modern cars. Since thermostats are now used in all makes of cars, a rough idea of ordinary solution temperatures may be obtained by noting the cooling system thermostat opening temperatures given for 35 models in Table 4.

TABLE 4

OPERATING TEMPERATURES OF FACTORY INSTALLED THERMOSTATS IN 1940 AND 1941 CARS

Number of Makes and Models	*Opening Temperature, °F.*
1	Below 145°
6	145°–150°
14	150°–155°
14	155°–160°

However, the data in Table 4 represent only minimum, theoretical, solution temperatures, since the fully open thermostat temperatures in these 35 models vary from 170 degrees to 185 degrees and, therefore, the true solution temperatures will be between these two sets of figures.

While the thermostat ratings give a fair idea of solution temperatures during normal cold weather driving, a 20-degree rise in solution temperature after the engine stops is permissible in satisfactory design, according to a leading automotive authority (*6*). It will, therefore, be evident that, if boiling is to be completely eliminated, it is necessary that the solution boiling point be at least 20 degrees higher than the normal operating temperature as determined by the thermostat. It is important to compare maximum coolant temperatures with the boiling points of commonly used anti-freeze solutions as given in Table 5.

TABLE 5

BOILING POINTS OF COMMERCIAL ANTI-FREEZE SOLUTIONS

	Boiling Points of Solutions at +10°	*0°*	*−10°*	*Freezing at −20°*
Methanol type	190°	185°	182°	179°
Ethanol type	187°	184°	182°	180°
Ethylene glycol type	218°	220°	221°	223°

When these boiling-point data are compared with the maximum solution temperatures previously discussed, the reason for the large boiling losses experienced with the so-called low-boiling anti-freezes is immediately apparent. Extensive field tests have shown that "after boil," resulting from the rise in solution temperature after shutting off the engine, is the major cause of solution loss rather than evaporation. The following test results show how serious overflow losses may be even in average car operation.

TABLE 6

ANTI-FREEZE OVERFLOW LOSS DATA IN RECENT MODEL TEST CARS

Test No.	*Thermostat Temp., °F.*	*Anti-freeze Type Used*	*Freezing Point Maintained*	*Test Duration*	*Overflow Loss, cc. per Month*	*Total Anti-freeze Used per Six Months gal.*
1	142°	Ethylene glycol	−40°F.	November to May	8	1.70
2	146°	Methyl alcohol	−40°F.	November to May	2350	3.21
3	166°	Ethylene glycol	−10°F.	November to May	0	1.95
4	158°	Methyl alcohol	−10° F.	March to April	6438	6.42

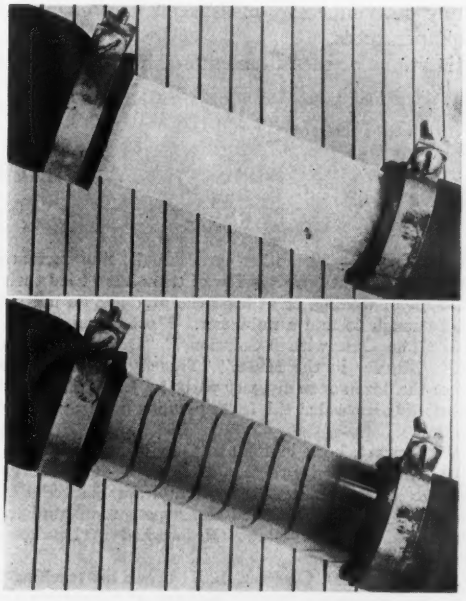


FIGURE 6.—COOLING SYSTEM AERATION IN UPPER RADIATOR HOSE CONNECTION

These test cars were normal in every way and no effort was made to select cars having high opening temperature thermostats, or cars which were particularly hard driven. Proper evaluation of the "after boil" problem with alcohol anti-freeze *cannot* be made solely on the basis of average overflow losses for any given test period, partly because the average loss will vary widely from one locality to another, and from one winter to another, depending on the climatic conditions, and partly because occasional large individual "after boil" losses do not show up clearly when the losses are averaged over an entire winter—although these individual losses can suddenly result in great inconvenience if the car driver is not aware of their occurrence. Thus, it is apparent that in the use of low boiling-point anti-freezes one must reckon not only with the cost of "after boil" replacements of solution, but with the necessity of frequently checking solution and making replacements.

THERMAL CONDUCTIVITY, COOLANT EFFICIENCY, AND HEAT TRANSFER

A further requirement of an acceptable anti-freeze solution is that its thermal properties be such as to permit optimum engine performance, that is to say, full power development with freedom from abnormal effects such as knocking, valve sticking, etc. The heat transfer characteristics of an anti-freeze solution in a cooling system, as estimated by measurements of solution thermal conductivity, specific heat or volumetric heat, viscosity and density, are sometimes considered to be a means of evaluating the effectiveness of a coolant in permitting optimum engine performance. Similarly, the heat transfer characteristics are sometimes experimentally determined by measurement of engine metal wall temperatures.

Estimations or measurements of heat transfer properties may be used to compare the cooling effectiveness of different anti-freeze liquids, but any differences so found are of no importance whatever unless it can be shown that they are large enough to be reflected as differences in engine performance. For this reason, precision full-scale engine dynamometer tests were made to determine the engine power output obtained with the three types of anti-freeze solution present in the cooling system. The test results showed no measurable differences in engine performance obtained when cooling the engine with solutions of methanol, ethanol, ethylene glycol, or with water.

In summary, it is concluded that ethanol and methanol solutions are satisfactory for automobile anti-freeze under operating conditions where overflow losses from boiling are not a problem, that all three of the commonly used anti-freezes should be effectively inhibited against corrosion, that ethylene glycol should be inhibited against foaming and creepage, and that of the three, inhibited ethylene glycol is the most nearly suited by its physical and chemical properties to meet all the coolant and anti-freeze performance demands of the modern engine. Furthermore, with the trend of present automotive design away from low engine operating temperatures(*5*, *7*) the comparatively high boiling points of ethylene glycol solutions over methanol and ethyl alcohol solutions offer a greater margin of safety than is generally appreciated.

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ALFRED WALTER STEWART

(Frontispiece)

MANY chemists, like other intellectuals, find recreation in detective stories, but probably few of them have tried their pens at this type of writing, or at least the products do not seem to be good enough to find a publisher. Most chemists who have enjoyed "The Case with 9 Solutions," "Death at Swaythling Court," "Murder in the Maze," "Tragedy at Ravensthorpe," or any of the dozen or so mystery yarns by J. J. Connington, will be surprised to learn that this is the pseudonym of a distinguished colleague.

A. W. Stewart, born in 1880 at Glasgow, received his B.Sc. in 1902 at the University there. After a year at Marburg under Zincke, he was appointed 1851 Exhibition Science Research Scholar, and in 1905 continued his investigations and training as Carnegie Research Fellow. He worked in London under Collie and Ramsay.

Dr. Stewart (Sc.D. Glasgow, 1907) began his teaching career in 1907 as Lecturer on Stereochemistry at University College, London. In 1909 he went to Queen's University, Belfast, as Lecturer on Organic Chemistry. He was called to his *alma mater* in 1914 as Lecturer on Physical Chemistry and Radioactivity, and remained until he was appointed to the Professorship of Chemistry at Queen's University in Belfast. He has occupied this chair with signal success since 1919.

He is the author of about forty research papers, mainly on spectrographic subjects. His prediction of isobarism among the elements was later verified by Aston by means of the mass spectrograph. He discovered the Teslaluminescence spectra of organic compounds and elucidated the relationships between these spectra and the chemical constitution of the compounds.

Professor Stewart's name has become familiar to a wide circle of chemists through his very excellent books: "Stereochemistry" (two editions); "Recent Advances in Organic Chemistry" (sixth edition in conjunction with Hugh Graham); "Recent Advances in Physical and Inorganic Chemistry" (six editions); "Chemistry and Its Borderland."

—Contributed by Ralph E. Oesper,
University of Cincinnati

The Study of Gaseous Dissociation as an Introduction to the Law of Mass Action[1]

GLEN WAKEHAM

University of Colorado, Boulder, Colorado

RECENT elementary texts tend to ignore the important phenomenon of gaseous dissociation. With some notable exceptions (*e. g.*, Deming[2]) they are likely merely to mention the fact that hydrogen iodide dissociates on heating, without any adequate explanation or discussion of the generality and theoretical and practical significance of the phenomenon.

Historically, the discovery of gaseous dissociation by St. Claire de Deville in 1857 solved several troublesome theoretical puzzles and opened the way for the general acceptance of Avogadro's Hypothesis. It also seems to have given Guldberg and Waage the first hint to the law of mass action.

It seems to the writer that, for several reasons, a study of gaseous dissociation offers the simplest and most convincing method of introducing equilibrium theory. First, the *fact* of gaseous dissociation can be easily and visually demonstrated, whereas ionic dissociation must be inferred from relatively indirect experimental evidence. The phenomenon is readily visualized in the student's mind, whereas it is not at all easy to devise a simple, valid picture of ionization. Equally important is the fact that the law of mass action explains completely and finally all the observed phenomena of gaseous dissociation, but applies—somewhat doubtfully—only to very dilute solutions of electrolytes. This is not to deny the necessity of applying the law of mass action to ionization theory. But as long as standard analytical texts tacitly ignore the theories of Debye, Hückel, and Brønsted and write equations with "H^+" ions after calmly admitting (in a fine-print footnote) that they don't exist—being in reality "oxonium" ions—it cannot be said that a final and completely satisfactory application of the law of mass action to solutions has been achieved. Hence I venture to plead for the use of gaseous dissociation as the simplest and most effective method of introducing the law of mass action. A further argument is the wide application of equilibrium theory to important industrial operations such as sulfuric acid manufacture and nitrogen fixation, furnishing plenty of practical examples.

The actual presentation may proceed somewhat as follows:

1. Experimental demonstration of the fact of gaseous dissociation: Heat hydrogen iodide and show the color change. The *reversible* nature of the reaction can be demonstrated by preparing a sample of HI sealed into a combustion tube at *low pressure* (about 10 mm.). At higher pressures, some of the free iodine will be precipitated on the walls of the tube. Dissociation with change of volume can be demonstrated in a Victor Meyer vapor density apparatus, with SO_3, NH_4Cl, or PCl_5, using boiling H_2SO_4 or mercury in the outside jacket.

2. In order to familiarize the student with the idea of dissociation, use problems in which the degree of dissociation is calculated from volumetric data. Work from first principles rather than from a formula derived algebraically. The volume of 0.1 g. of PCl_5, at 290°C. (b. p. of H_2SO_4) is found, in the vapor density apparatus, to be actually 48 cc. The theoretical volume (if the gas were not dissociated) is easily calculated to be 26 cc. The *increase* of the observed over the "theoretical" is therefore $\frac{48 - 26}{26}$ or *about* 85 per cent. As *one* molecule of PCl_5 dissociates into *two* molecules (one each of PCl_3 and Cl_2) it is clear that the degree of dissociation is 85 per cent. A parallel experiment with SO_3 demonstrates that the degree of dissociation in this case is *twice* the increase in volume. Most beginning students are unable to follow the algebraic derivation of the formula:

$$\gamma = \frac{V - V_1}{(n-1)V_1}$$

But they can "see" from some such diagram as the following one why it is that, in the case of PCl_5, the degree of dissociation equals the observed *increase* in volume over what the "normal" or undissociated volume would be under the same conditions; why the dissociation of HI produces *no* increase in volume over the "normal"; and why, in the case of SO_3, the degree of dissociation is *twice* the observed increase in the volume over the "normal." (See chart.)

The next step is the introduction of the law of mass action, treated as an empirical discovery, but demonstrated theoretically on the basis of the following four concepts: Reaction Velocity, Concentration, Reversible Reaction, and Equilibrium.

In defining reaction velocity, some authors (*e. g.*, Holleman[3]) try to smuggle in the calculus, which is quite unintelligible to the average freshman. As this function cancels out in the mathematical demonstration of the equilibrium constant, it is surely sufficient to define it, non-rigorously, as the *average* velocity during a short interval of time.

[1] Presented before the Division of Chemical Education at the 101st meeting of the A. C. S., St. Louis, Missouri, April 8, 1941.

[2] DEMING, "Fundamental chemistry," John Wiley and Sons, Inc., New York City, **1940**, pp. 398–409.

[3] HOLLEMAN, "A text-book of inorganic chemistry," translated by COOPER, 7th ed., John Wiley and Sons, Inc., New York City, **1939**, pp. 76–7.

CHART SHOWING DIFFERENT TYPES OF GASEOUS DISSOCIATION

Assume, in each case, a degree of dissociation of 40% (0.4). Use, in each case, *ten* molecules of the dissociating substance.

First Type, monomolecular: $PCl_5 = PCl_3 + Cl_2$

Six molecules, *i. e.*, 60%, or 0.6, remain undissociated. $\{PCl_5\ PCl_5\ PCl_5\ PCl_5\ PCl_5\ PCl_5$

Six molecules plus four molecules plus four molecules equal fourteen molecules, in place of the original ten, so that the *increase* in number of molecules (*i. e.*, *increase* in volume over the "normal") equals exactly the *degree* of *dissociation*.

$PCl_5\ PCl_5\ PCl_5\ PCl_5$ *Four* molecules, *i. e.*, 40%, or 0.4, dissociate, producing: $PCl_3\ PCl_3\ PCl_3\ PCl_3$ *four* molecules of PCl_3, and: $Cl_2\ Cl_2\ Cl_2\ Cl_2$ *four* molecules of Cl_2

Second Type, bimolecular reaction without change in volume: $2HI = H_2 + I_2$

Six molecules, *i. e.*, 60%, or 0.6, remain undissociated. $\{HI\ HI\ HI\ HI\ HI\ HI$

Six molecules plus two molecules plus two molecules equal ten molecules, which was the original number, so that in this type of dissociation there is *no* increase in the number of molecules (*i. e.*, in volume) due to dissociation.

$HI\ HI\ HI\ HI$ *Four* molecules, *i. e.*, 40%, or 0.4, dissociate, producing: $H_2\ H_2$ *two* molecules of H_2, and: $I_2\ I_2$ *two* molecules of I_2

Third Type, bimolecular reaction with change in volume: $2SO_3 = 2SO_2 + O_2$

Six molecules, *i. e.*, 60%, or 0.6, remain undissociated. $\{SO_3\ SO_3\ SO_3\ SO_3\ SO_3\ SO_3$

Six molecules plus four molecules plus two molecules equal twelve molecules, or an increase of two molecules over the original ten. Thus, in this case, the *increase* in the proportion of molecules due to dissociation (*i. e.*, the increase in volume) is equal to *half* the degree of dissociation, or, conversely, the degree of dissociation is equal to *twice* the increase in volume due to dissociation.

$SO_3\ SO_3\ SO_3\ SO_3$ *Four* molecules, *i. e.*, 40%, or 0.4, dissociate, producing: $SO_2\ SO_2\ SO_2\ SO_2$ *four* molecules of SO_3, and: $O_2\ O_2$ *two* molecules of O_2

Many students confuse *equilibrium* with *equality*. The following "social" illustration will amuse any freshman class and may make clear the *dynamic* aspect of equilibrium: Imagine a dance hall with a hundred couples dancing. This system is in a sort of equilibrium, but is not static. At this juncture it is announced that refreshments are ready, in another room. The equilibrium is disturbed. Some of the partners separate and move toward the refreshment room. The initial reaction velocity is all in this direction.

After a few minutes, however, some of the dancers will return to the dance hall, rejoin each other, and resume dancing. This represents the "back reaction" of a reversible system. In time a sort of equilibrium is reached—the number of partners separating and leaving the hall in any unit of time will equal the number of couples going back to dance again. This equality of reaction velocity to and from the dance hall and the refreshment room represents dynamic chemical equilibrium. It is not likely that equal *numbers* of couples will be in each room. The system will work smoothly only if equal numbers pass in each direction in any unit of time.

We are now ready for the Law of Mass Action: $V \propto C$. In most elementary classes it will be necessary to explain the nature of variation by means of some simple illustration; *e. g.*, if one workman earns five dollars a day, two will earn ten dollars a day, three will earn fifteen dollars, etc. In this way the function of a *constant* (5) can be made clear, also the fact that a variation expression can be converted into an algebraical equation by the insertion of a constant.

Perhaps the chief objective of this treatment is to get the students to see how *all* chemical reactions are governed by the law of mass action and to comprehend something of the almost miraculous potency of constants in controlling the course of any reaction. To this end, the following ultimately simple derivation of the "concentration equilibrium constant" is offered.

Let A and B be any two chemical systems, one of which is convertible into the other. Then:

Reaction velocity "A" varies as Concentration "A," and
Reaction velocity "B" varies as Concentration "B."

Converting these expressions into equations by the insertion of constants, we get:

Reaction velocity "A" equals k_1 times Concentration "A," and
Reaction velocity "B" equals k_2 times Concentration "B."

But at "equilibrium" (explained above), Reaction velocity "A" *equals* Reaction velocity "B," hence k_1 times Concentration "A" equals k_2 times Concentration "B."

It is usually necessary to explain that this does *not* mean that k_1 equals k_2, or Concentration "A" equals Concentration "B," for students at this stage are all too prone to apply the famous axiom: "Everything equals everything else."

The algebraic transformation of the expression:

$$k_1 \times C_A = k_2 \times C_B \text{ into } \frac{C_B}{C_A} = \frac{k_1}{k_2} = K$$

will need to be carefully explained. It must also be pointed out that if $A \propto B$ and $A \propto C$, then $A \propto B \times C$. The definition can then be generalized: in any reversible reaction, $A + B + C \ldots = X + Y + Z \ldots$, the quotient:

$$\frac{\text{Conc. of } X \times \text{Conc. of } Y \times \text{Conc. of } Z}{\text{Conc. of } A \times \text{Conc. of } B \times \text{Conc. of } C}$$

is called the concentration equilibrium constant, it being merely a convention to divide the right-hand product by the left-hand one. If the teacher plans to use bimolecular reactions as illustrations, it must be explained that these concentrations must be "squared"; but it is not easy to show the reason for this to a non-mathematical class and, as far as the main objective of this presentation goes, the difficulty can be side-stepped by using monomolecular reactions only.

The student can now easily calculate a number of concentration equilibrium constants, from dissociation data either furnished by the teacher or looked up in a handbook.

The practical use of this theory will be clear to the student only if he is required to work back from some numerically simple constant and calculate the effect of the addition or removal of one of the products of a dissociation reaction originally at equilibrium. In order to save the non-professional, "cultural" student

from unnecessary numerical entanglements, the following simplifications can be used:

All temperatures should be multiples of 273, *i. e.*, 546°C., 819°C., 1092°C., 1365°C., etc.

Instead of using gram molecular quantities, unconventional but perfectly valid constants can be obtained starting with 1/22.4 of a gram molecule, the theoretical volume of which will be, of course, one liter at N.T.P. (S.T.P.).

Or, the numerically troublesome "22.4" factor can be eliminated by using "pressure equilibrium constants" instead of "concentration equilibrium constants."

The teacher using this introduction for the first time should be careful not to impose on his classes problems leading to cubic or bi-quadratic equations. Most elementary students have at least heard of the equation:

$$x = \frac{-b \pm \sqrt{b^2 - 4ac}}{2a}$$

but it is not wise to ask them to go beyond this.

It is the writer's experience that the majority of "cultural" chemistry students get a better idea of chemical equilibrium and the universal significance of the law of mass action from this presentation than when they are plunged directly into the theory of ionic dissociation. From the viewpoint of heuristic pedagogy, it is natural to expect the average student to understand more easily the theory which was developed first. The student who masters the idea of gaseous dissociation, with its chief implications, usually has no difficulty with ionic dissociation. And the more intelligent student is highly intrigued, even fascinated, by the discovery that, once he knows the constant, he can calculate and predict the quantitative effect, upon a gaseous system at equilibrium, of the addition or removal of a given amount of one of the dissociation products.

SOME PROBLEMS

1. The volume of one gram molecule of NH_4Cl at normal pressure and 273°C. is found to be 67.2 liters. Calculate the degree of dissociation.

2. One liter of CO_2 gas is measured at N.T.P. The gas is then heated to 1365°C., at normal pressure, and the volume is found to be eight liters. Calculate the degree of dissociation.

3. In Problems 1 and 2 calculate (*a*) the concentration equilibrium constants and (*b*) the pressure equilibrium constants.

4. Nine grams (approximately $^1/_{22.4}$ gram molecule) of PCl_5 is heated to 546°C. at N.P. and is found to occupy a volume of four liters. Without allowing the volume to change, 3.17 grams ($^1/_{22.4}$ gram molecule) of chlorine are added to the system. How will the concentrations of the various gases present be altered when equilibrium is reached?

5. How will the various concentrations be altered in the system in Problem 4 if the addition of chlorine is made at constant pressure instead of at constant volume?

6. What will happen, quantitatively, to the system described in problem 4 if half the free chlorine present is *removed* (*a*) at constant pressure, (*b*) at constant volume?

7. What would happen if *all* the free chlorine were removed?

● Watson Davis, Director of Science Service, brought out some points in a recent luncheon talk that are well worth emphasizing.

Creative and aggressive application of science is called for to meet the present emergency. Research, experimentation, and invention are as important to national defense as the airplanes, ships, tanks, and guns used by the military forces. In a large measure the weapons and the means of protection against weapons are created by science.

New organizations have been created to do research for the military forces. There is the National Defense Research Committee which has over 200 secret projects underway. These involve the science facilities at 80 of our large universities and personnel at 30 large industrial laboratories. It is estimated that a fourth of the physicists of the nation are in defense research and many of them are working on NDRC projects. The Army and Navy undertake much research directly but in these urgent times the normal military research of the nation has been increased many fold by the extensive organization of projects under the NDRC.

● The National Inventors Council, located in the Department of Commerce in Washington, has assumed the responsibility for receiving and evaluating any suggestions which may be offered by the public to help our national defense effort. They have already received many thousands of suggestions, some of which are already being put to use by the Army and Navy. There is always a chance that someone's "hunch" may prove vital, and the Council will see that every one is judged fairly.

● The Bakelite Corporation (30 East 42nd Street, New York City) has some educational lecture exhibits which they are willing to loan to educational institutions for short periods of time. They tell briefly the raw material, manufacturing, and finished product stories of the different types of modern bakelite and vinylite plastics. They are in sturdy wooden cases, two feet square, which can be shipped safely and easily. Anyone interested in borrowing one of these exhibits can arrange to do so by writing the editor of the *Bakelite Review* (mentioning the JOURNAL OF CHEMICAL EDUCATION) and indicating the exact date the exhibit is wanted.

Specialized Chemistry in Secondary Education[1]

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THERE is a definite movement to require the teaching of science in elementary schools. A study of the offerings indicates that the students entering the junior high school may have some information concerning the biology and physics fields but certainly little information about the field of chemistry.

In many school systems general science is a core subject of the junior high school curriculum. Leker (*1*) shows that most of the subject matter is from the biology field, less from the field of physics, and very little from that of chemistry. Davis (*2*), studying eight widely used general science textbooks, lists air, water, and food as important topics which may be classed as chemistry. These studies indicate that general science also contains some information about astronomy, geology, and weather. The work is taught by the textbook-recitation method supplemented by some demonstrations. There is almost never any laboratory work.

An unpublished survey of science instruction in the Senior High Schools of New Jersey indicates that over forty-eight per cent of the tenth grade, thirty-four per cent of the eleventh grade, and thirty-nine per cent of the twelfth grade children take some science. This study also shows biology to be a five period per week subject in seventy per cent of the classes. Less than one-third of the physics and chemistry classes had as few as five periods per week.

High-school chemistry and physics survive because they have been of value to those who went to college and because they were of practical value to those who went directly into industry. That high-school chemistry is of value as preparation for college chemistry has been shown by the studies (*3*, *4*) made of the Coöperative Chemistry Test results. In high schools large enough for segregated classes the present specialized chemistry courses serve a useful purpose and are elected by students who expect to go to college. However, study should be made of the exact contributions of high-school chemistry to college chemistry so that dead wood may be eliminated. A large majority of high-school students do not receive any chemistry, but elect other subjects which they consider of more value.

A high-school course in chemistry for all children can be justified upon other grounds:

1. The discoveries in the area of chemistry are having far-reaching effects upon the social, economic, political, and moral environment of everyone.
2. A knowledge of chemistry is necessary for care of the health.
3. An understanding of chemistry is needed by the masses if they are to continue to support research and specialized training by expenditure of public funds. College chemistry enrolment would be drastically reduced if this support were withdrawn.
4. No other existing science course covers the chemistry area, although a knowledge of it is of increasing fundamental importance to even semiskilled workers in agriculture and industry.

This chemistry course for all children should enable the individual to:

1. Understand himself and his environment.
2. Understand how to control and modify his environment.
3. Understand how chemical discoveries have modified the social, the economic, the political, and the cultural institutions of our world.
4. Understand how the chemist works.
5. Understand the contributions of the chemist in controlling the health of the community.
6. Know when to seek the services of the chemist and not rely upon his own skill.
7. Understand and use the steps to scientific or reflective thinking.

A committee (*5*) of the Division of Chemical Education recommended a core of fundamentals at the Milwaukee meeting. This core would not require more than half the high-school year and would leave time to develop ideas in chemistry of value in general education. In the past, lists of minimum essentials have been maximal rather than minimal. In attempts to cover these "essentials" high-school students have been exposed to every idea of general college chemistry, with disappointing results. College teachers of chemistry would welcome such a core of fundamentals upon which they could depend and build. Such a general course would relieve the colleges from presenting an orientation course in chemistry and thereby permit more time for teaching specialized courses. The details of such a course should be the concern of high-school teachers of chemistry who have an adequate background in chemistry and who also understand and accept the aims of secondary education.

In many schools where such a general chemistry course has been offered, little or no laboratory work is included. This is due to incorrect interpretation of experimental data by unscientific generalists and to a desire to save funds. The outcomes of laboratory instruction are not generally understood or appreciated,

[1] Presented as part of a panel discussion on The Future of Chemistry as a Specialized Science in the High-School Curriculum, before the Division of Chemical Education at the ninety-ninth meeting of the A. C. S., Cincinnati, Ohio, April 9, 1940.

for they do not lend themselves to measurement by written examinations. But they are always apparent when students attempt to do laboratory work in college. Laboratory work in high-school chemistry is frequently the only supervised laboratory work which a student experiences. Such laboratory should teach the fundamental operations and should emphasize the discovery of new facts rather than the mere verification of textbook statements.

High-school teachers should study the problems:

1. What are the fundamental laboratory operations which a general chemistry student should be able to carry out?
2. What can best be demonstrated and what must be performed by students themselves?
3. How can the laboratory be used to acquire information not in the textbook but considered by the students to be of value?

Why not use a portion of the time devoted to chemistry laboratory to pursue applied chemistry in some of the following ways:

1. Practice in photography. There are many chemical applications in photography, and it is considered of value by children.
2. Application of chemistry to testing, both qualitatively and quantitatively, for the presence of substances. There is an element of a game in this. The analysis of vinegar, household ammonia, milk, etc., requires real chemical skill and has absorbing interest.
3. Apply chemistry to testing for the constituents, both harmful and useful, in commercial preparations: Which dentifrices contain soap? What is in a depilatory? What besides sodium chloride is in table salt?
4. Perform dye experiments. The detection of a dye in food fascinates students. High-school and college laboratory manuals have hardly touched the possibilities of this field.
5. Ascertain under what conditions metals will corrode. How can one determine the hardness of metals? Such units have been worked out and many others can be prepared.

There is an effort being made to combine physics with chemistry in a one-year course and call it physical science. In most cases this course is offered to the non-college students who cannot profit by college preparatory work.

Personal observation indicates that these courses are not so promising as they appeared upon paper and in many cases are a distinct disappointment to those teaching them. The one-year courses usually have no laboratory work and do not appear to be challenging to pupils. In most cases they offer few activities which pupils desire. They do not attract the better pupils but serve as concentration camps for "problem" students. These courses require the efforts of the most capable teachers in the science department, who must be trained thoroughly in chemistry, physics, and biology. Under proper conditions these courses can be made attractive.

There is a need for a general chemistry course in a twelve-year program. Such a course should be organized so that its aims harmonize with those of secondary education. It should be designed to offer opportunity for pupil participation and activity, and its outcome should be an understanding of the environment and the conditions under which it can be controlled and modified.

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(3) PHELAN, J. CHEM. EDUC., **14**, 589 (Dec., 1937).
(4) REED, *ibid.*, **16**, 187 (April, 1939). [Further studies have been made: MARTIN, *ibid.*, **17**, 70 (1940) and FOSTER, *ibid.*, **18**, 159 (1941).]
(5) "Minutes of the annual business meeting of the Division of Chemical Education," *ibid.*, **15**, 545 (Nov., 1938).

LETTERS

Less Ammonium Chloride

To the Editor:

Two interesting accounts [DAVIS AND NECKERS, "An ammonium chloride chimney," J. CHEM. EDUC., **18**, 292 (1941), and "Out of the editor's basket," *ibid.*, **18**, 347 (1941)] have recently appeared in this journal regarding ammonium chloride growths. Most chemists, however, are continually annoyed by the accumulation of ammonium chloride deposits on bottles and equipment around chemical laboratories and stock rooms. Bottles of concentrated acids and of ammonium hydroxide are usually coated with heavy and unsightly layers of ammonium salts after storage of a few days or weeks. This nuisance can be largely eliminated by proper storage of these concentrated reagents. Most stock rooms have shelves, one above the other. The concentrated acids and bases may be stored on separate shelves, the one of least density on the highest shelf, and the one of greatest density on the bottom shelf. Such an arrangement will reduce the accumulation of these unsightly deposits to a minimum.

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Out of the Editor's Basket

SOME time ago, Professor E. R. Washburn, of the University of Nebraska, sent us the results of a little "study" of the comparative performance of students with and without high-school chemistry. The question whether the "carry-over" or advantage of high-school chemistry persists into elementary college chemistry, at least beyond the first semester, has been frequently asked. Since the answers have often been doubted, any additional evidence will be welcomed. A follow-up course in elementary chemistry has been given at Nebraska for a number of years, which begins in the second semester and finishes in the first semester of the following year. Only about one-third of the students in this course had had high-school chemistry but during the last twelve years 86 per cent of this group passed the course, while only 77 per cent of those without high-school preparation passed. Furthermore, a larger proportion of the former group than of the latter received grades above 80 during both semesters. While the conditions were not carefully enough controlled for accurate educational measurements, still the results of the analysis of these grades may be of some significance.

● You need never suffer from the lack of a fume hood if you have a suction pump at hand. Robert J. Bibbero, of the Pacific Manifolding Book Company, Emeryville, California, sends in a suggestion which may not be entirely original but is a good one. If the flask, beaker, or casserole over the burner is obnoxious the fumes can be removed by clamping a large funnel over it, inverted, and attaching the stem to the suction pump.

● An adjustable thermometer support, for use in a distilling flask or elsewhere, is described by O. L. Baril, of Holy Cross College. The idea will probably be new to some. Through a one-holed stopper in the flask is inserted a short piece of glass tubing through which the thermometer will just pass easily. A short piece of rubber tubing over the upper end of the glass tube will hold the thermometer firmly but will still permit it to be pushed up and down for adjustment.

● Rumor has it, according to Dr. Russell M. Wilder, of the Mayo Clinic, Chairman of the National Research Council's nutrition committee, that the Nazis are making deliberate use of thiamin starvation to reduce the populations of the occupied countries to a state of depression and mental weakness and despair which will make them easier to hold in subjection. The part that thiamin, or vitamin B_1, plays as a "pepper-upper" or general protector against irritability, depression, and exhaustion, seems to be one of the recent developments in the field of nutrition.

● We have just received a copy of an "Outline for Semimicro Analysis of Cations" by L. A. Munro and J. A. Pearce, of Queen's University, Kingston, Ontario. It is of a "flow sheet" type for student use in two colors and contains in addition a considerable amount of information about solubilities, flame tests, special reactions, etc. While the outline follows in general the scheme of macro analysis, it is another example of the increasing popularity of the semimicro technic.

● From the Bridgeport Brass Company we have some information concerning brass and the national defense needs. It seems that the demands of the national defense program have produced a temporary scarcity of certain essential metals. The large quantity of zinc required in defense work has made it increasingly difficult to obtain brass for ordinary commercial uses. As a result, considerable interest has arisen in the possibility of substituting alternative materials for brass during the emergency period. This is particularly true in the case of high brass, because of its high zinc content.

While the use of other copper alloys containing a lower percentage of zinc is helpful, it is better from the broader material outlook to consider the use of pure copper. The use of copper eliminates both the need of another alloying metal and the necessity of remelting to produce the alloy. Up to the present time, the shortage of copper is only less acute than that of zinc.

● We also learned some other interesting things about the use of aluminum in copper-zinc alloys. Years ago the addition of aluminum to the copper-zinc alloys would never have received serious consideration. Today aluminum is an essential raw material in all brass mills.

The original reluctance to use aluminum was caused by the heavy oxide film which it forms on the surface of molten metal. So strong was this reluctance that the danger of contamination of other scrap by scrap aluminum-bearing alloys was considered to be a sufficient reason for avoiding the manufacture of aluminum-bearing alloys.

Improved methods in the casting shop have completely eliminated this former difficulty. While aluminum still forms a film, means have been developed which enable the casting shop to produce sound metal in spite of the film, and aluminum additions in copper-zinc alloys are now regularly employed to obtain specific advantages.

The more recent developments in the use of aluminum additions, however, have been the result of precisely the same property that formerly limited aluminum's usefulness—its ability to form strong, tenacious

oxide films. This property is especially advantageous in combating certain types of corrosion, particularly in condenser tubes. Condenser tube corrosion has increased in recent years because of increased water speeds, with the resulting turbulence and entrapped air. The addition of aluminum increases the strength of the protective film formed, and thus increases resistance to erosion by the high velocity of the water.

RECENT BOOKS

STARCH AND ITS DERIVATIVES. *J. A. Radley*, M.Sc., A.I.C. Volume XI of a Series on Applied Chemistry, *E. H. Tripp*, Ph.D., Editor. D. Van Nostrand Co., Inc., New York City, 1940. x + 346 pp. 28 figs. 61 photomicrographs. 14 × 22 cm. $6.00.

The English author states, in the preface, that this book seeks to summarize recent progress in an important domain of chemical industry. It does that. The book is divided into four parts: I. The Structure and Reactions of Starch; II. The Manufacture of Starch and Starch Products; III. The Industrial Applications of Starch and Starch Products; and IV. The Examination and Analysis of Starch and Starch Products. Sixty-one photomicrographs of starch, obtained with plain and polarized light, and both subject and author indexes are included in the 346 pages. Typographical errors are few in number.

The author has done well in trying to fulfil his purpose of recording the scientific and technological results in an extensive field. About 100 pages are devoted to the history, latest developments regarding structure, physical and chemical characteristics of starch, and a section concerning ethers and esters of starch, which deals with compounds of much interest at the present time. The manufacture of root and cereal starches, because of books already available, is discussed very briefly. Although the potato is an underground stem tuber it is considered as a root. Starch content of white potatoes (page 103) as an average, in Germany, is about 18 per cent instead of 25–40 per cent, as stated. There is very little reference to sago starch. Starch products are discussed extensively.

Since there are marked differences in the chemical and physical behavior of starches from different sources, obtained by different methods, other than granule shape and size, it is now desirable to stress the source of starch. This information is sometimes omitted. A European would probably think mostly in terms of potato starch; an American, of corn starch; and an inhabitant of Java, of manioc starch (tapioca or cassava).

There are four to seven chapters for each of the four parts, with an extensive bibliography at the end of each chapter. This feature makes it a very valuable general reference book for starch chemists.

Topics such as uses and products of starch are treated more exhaustively than in most books of this size. It is evident that the author undertook to assemble an extensive number of topics pertaining to the science and technology of starch.

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THE MANUSCRIPT. A GUIDE FOR ITS PREPARATION. Third Edition. John Wiley and Sons, Inc., New York City, 1941. xvi + 75 pp. 16 figs. 15 × 23 cm. $1.00.

This monograph gives specific directions, from a technical viewpoint, for the preparation of copy for the printer; directions for the selection, preparation, and shipping of illustrations; details as to the completion of the manuscript, with suggested layout, preparation of front matter, problems, exercises, appendix, glossary, and index; instructions for the handling of proof; and a brief paragraph on formal publication and copyright regulations. It is strictly practical, bringing up points which may cause difficulty if not attended to properly, and should promote understanding between author and publisher.

CHEMISTRY OF FOOD AND NUTRITION. *H. C. Sherman*, Ph.D., Sc.D., Mitchill Professor of Chemistry, Columbia University. Sixth Edition. The Macmillan Company, New York City, 1941. x + 611 pp. 46 figs., 65 tables. 14 × 21 cm. $3.25.

As every one interested in nutrition probably knows, this book has been widely used as a text for a generation. It is intended for college classes and presupposes a knowledge of general and organic chemistry. It presents the experimental facts, summarized and evaluated, which furnish the basis for the science of nutrition and its practical applications.

This edition may truthfully be called a revision because a considerable part of the book has been rewritten. Three new chapters on the recently discovered vitamins have been added and the valuable references and selected readings at the end of each chapter have been carried through 1940.

Because of the historical value of this book, it may be of interest to others, as it was to the reviewer, to compare this with the first edition which appeared in 1911. In the introduction to the first edition Doctor Sherman practically summarized the state of our knowledge of nutrition at that time when he said that the nutritive value of food "as a source of energy for maintaining the work of the body and of material for preventing or replacing the waste of the body substance or for growth, is chiefly judged (1) by its chemical composition, (2) by its behavior in digestion, (3) by its behavior in metabolism." Later on there was a statement of a prophetic nature in which he said: "It is becoming more and more apparent that even among staple foods there are many cases in which the ordinary routine analysis fails to differentiate substances which are quite different in nutritive value. It is not safe to conclude, as is sometimes done, that these are 'differences which chemistry cannot show' for chemistry can show vastly more than is shown by the partial analyses usually made."

How true this statement has proved to be may be shown by a brief comparison of the contents of the first and last editions. The material included in the first fifteen chapters of the 1941 edition constitutes approximately the entire subject matter of the 1911 edition. The next fifteen chapters of the latest edition, including eight chapters on the vitamins, present the new Chemistry of Food and Nutrition as it has developed in three decades. In the edition of 1911 no mention was made of rickets as a specific dietary deficiency disease. The necessity for an adequate supply of calcium for development of the skeleton of growing children was stressed, but there was no question of the need of any factors other than liberal allowances of calcium and phosphorus in the diet. Mention was made of an epidemic of scurvy in a British garrison during the seige of Ladysmith but it was thought that the disease followed the consumption of a diet containing too little of the base-forming elements. Thus scurvy was recognized as related to diet but the dietary constituents thought to be responsible were the mineral elements known to occur most abundantly in fruits and vegetables. Many other interesting comparisons might be made but space does not permit.

All teachers who have depended upon this book for class use will be grateful that this concise history of the development of scientific nutrition has been brought up to date and the new material presented in the same unbiased manner which is so characteristic of the author.

RUTH JOHNSTIN

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THE CHEMISTRY OF POWDER AND EXPLOSIVES. Volume I. *Tenney L. Davis*, Ph.D., Professor of Organic Chemistry, Massachusetts Institute of Technology. John Wiley and Sons, Inc., New York City, 1941. xi + 216 pp. 50 figs. 13.5 × 21.5 cm. $2.75.

The author, a well-known authority in the field of powder and explosives, says in the preface to this book: "The book has been written for the purpose of informing chemists, already well trained, concerning the modes of behavior of explosive substances and concerning the phenomena, both chemical and physical, which they exhibit. No effort has been made to describe the use of explosives in ammunition and in blasting beyond the minimum of description which is needed to make clear the modes of their behavior, and no account has been included of the chemical-engineering aspects of their manufacture."

The chapter headings are: I. Properties of Explosives, II. Black Powder, III. Pyrotechnics, IV. Aromatic Nitro Compounds.

The national emergency and the efforts on the part of the United States Government to train qualified chemists in explosives make this book a very welcome addition to the small family of texts on the subject. Workers in the field wait impatiently for Volume II which is rapidly nearing completion.

In Chapter I the author defines and classifies explosives, discusses the events occurring during the firing of a round of ammunition, and briefly describes some tests of explosive force (brisance), velocity of detonation, and sensitivity. Chapter II contains much valuable material on black powder. In modern ammunition the use of black powder is confined to fuses and igniters and seldom has the subject been treated as completely as it is here. The long chapter on pyrotechnics, while interesting, complete, and undoubtedly valuable, seems to break the continuity of the text by injecting toys into the very center of an otherwise serious topic—military explosives. It would seem that this chapter might best be segregated and abbreviated. The last chapter is excellent and probably the most complete treatment of the subject of explosive aromatic nitro compounds to be found anywhere.

In the interest of national defense and to help those men being trained as inspectors of explosives, the reviewer would like to see included a chapter describing some of the practical uses of explosives in ammunition and a more detailed discussion of the tests of the powders, finished rounds, and components.

The topics to be presented by the author in Volume II are: nitric esters, smokeless powder, dynamite and other high explosives, ammonium nitrate and nitro amines, primary explosives, detonators and primers.

A. T. BURTSELL

COLLEGE OF THE CITY OF NEW YORK
NEW YORK CITY

THE PHARMACOLOGY OF ANESTHETIC DRUGS. *J. Adriani*, M.D., Instructor in Anesthesia, New York University College of Medicine; Assistant Visiting Anesthetist, Bellevue Hospital, New York. Second Edition. Charles C. Thomas, Springfield, Ill., and Baltimore, Md., 1941. ix + 86 pp. 21.3 × 26.9 cm. $3.50.

Condensed to the essentials, this volume is illustrated with outline diagrams focusing attention on physiological and pathological changes that occur in various organs and systems under the influence of anesthetic drugs. The style is that of brief notes rather than a connected narrative. The contents include: effects of physical and chemical properties on pharmacological activity; absorption and elimination; general systemic effects; disturbances of respiration; a consideration of the various types of anesthetics (gaseous agents, volatile agents, aliphatic nonvolatile agents, barbiturates, local anesthetics, opiates); nonanesthetic drugs and inorganic gases used in conjunction with anesthesia; some clinical considerations. Following the main portion of the text are a table of atomic weights and conversion factors, a table of usual doses, and qualitative tests. The bibliography is useful for further references.

HANDBOOK FOR CHEMICAL PATENTS. *Edward Thomas*, A.B., Chemical Patent Attorney. Chemical Publishing Co., Inc., New York City, 1940. x + 270 pp. 14 × 21 cm. $4.00.

This second book on patent law, by the author of "The Law of Chemical Patents" (1938), reviews the fundamentals of patent law and explains them in the light of the changes that have taken place since the middle of 1937. It is written so that an interested reader may appreciate the underlying philosophy of patent law, while at the same time it is a ready reference book for the attorney or for the research chemist. Chapters on specification writing, anticipation, infringements, and patent evidence are exceptionally thorough and clear. Over 1200 citations to cases in the patent literature are given and these cases and citations are conveniently cross-referenced.

This book is valuable alone but it is still more so when used with "The Law of Chemical Patents."

WILLIAM F. O'CONNOR

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NEW YORK CITY

FORENSIC CHEMISTRY. *H. T. F. Rhodes*, Dip.Inst.C. (Lyon), Correspondent of the International Academy of Criminology; Honorary Research Assistant in the "Conan Doyle" Laboratory of Chemical Research, Department of Technical Police, Prefecture of the Rhone, France. Chemical Publishing Co., Inc., New York City, 1940. viii + 214 pp. 13.5 × 21.5 cm. $5.00.

According to the author, "the subject of forensic chemistry is one which does not figure largely in the chemical literature so that there would seem to be room for a text book on the subject. The special characteristic of this one is that the subject matter is strictly confined to formally chemical theory and technique."

The author has had the two objectives of collecting together the information scattered throughout the criminological literature and of outlining procedure in a forensic chemical laboratory. The book first takes up the application of chemical methods to the identification of the person, such as the study of skin prints, occupational dust (both inorganic and organic), blood groups, and seminal stains. The application of chemical methods to the proof of *corpus delicti* includes analysis of stains, study of firearms and explosives, chemical examination of questioned documents, of counterfeit money, and of toxic agents.

The book contains a suggested list of references, largely to foreign publications. It is systematically and logically organized with bold-face headings marking the divisions of subject matter. It should be of interest to those who wish to know more about the practical application of laboratory procedures to this particular type of work.

UNIVERSITY PHYSICS. *F. C. Champion*, M.A., Ph.D. (Cantab.), Lecturer in Physics, University of London. Blackie and Son, Ltd., London and Glasgow, 1940. (Interscience Publishers, Inc., New York City.) Part I. General Physics—157 pp. 108 figs. 14.5 × 21.8 cm. $1.50. Part II. Heat—148 pp. 83 figs. 14.5 × 21.8 cm. $1.50.

Primarily intended for students taking a first- and second-year course in physics at a university, this book deals in the first volume with general physics, including kinematics, dynamics of a particle, statics and dynamics of a rigid body, units and dimensions, the acceleration due to gravity and the gravitational constant, gyroscopic motion, elasticity, hydrostatics, properties of gases and vapors, properties of liquids at rest and in motion. The treatment is fairly mathematical, and problems and answers are given at the end.

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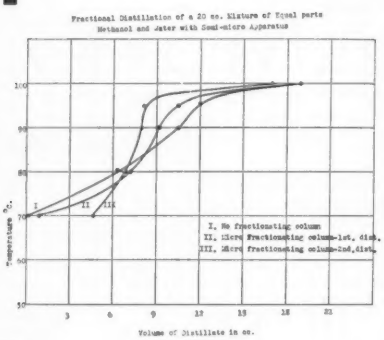
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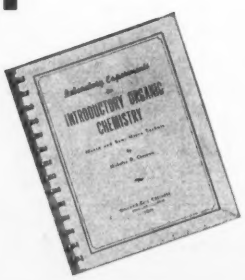

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Miniature a-c and d-c voltmeters and ammeters in the two inch classification for general use are described in a new 12-page bulletin announced by *Westinghouse Electric and Manufacturing Company.* Full scale readings on the d-c ammeter series are from 20 microamperes to 100 amperes and on the a-c units, from 5 milliamperes to 50 amperes. Voltmeter calibrations are from 5 millivolts to 1000 volts full scale on both a-c and d-c lines.

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A copy of catalog section 43-330 may be secured from department 7-N-20, *Westinghouse Electric and Manufacturing Company, East Pittsburgh, Pennsylvania.*

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New Bulletin on Two-Lens Quartz Spectrograph

A new twelve-page bulletin on the Gaertner Two-Lens Quartz Spectrograph has just been published by *The Gaertner Scientific Corporation, 1201 Wrightwood Avenue, Chicago, Illinois.*

The Bulletin contains twelve pages of detailed description and illustrations of the Spectrograph and its component parts. Some of the more important accessories are also described and illustrated.

Copies of this bulletin are available upon request to the Gaertner Scientific Corporation.

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